

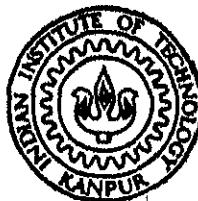
SULFUR MEDIATED INDUCED ELECTRON TRANSFER REACTIONS IN THE CHEMISTRY OF THIOTUNGSTATES

by
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DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR
OCTOBER, 1986

✓ **SULFUR MEDIATED INDUCED ELECTRON TRANSFER
REACTIONS IN THE CHEMISTRY OF THIOTUNGSTATES**

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

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by
MOHD ASIM ANSARI

to the
DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR
OCTOBER, 1986

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STATEMENT

I hereby declare that the matter embodied in this thesis "Sulfur Mediated Induced Electron Transfer Reactions in the Chemistry of Thiotungstates," is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor S. Sarkar.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



Mohd. Asim Ansari

Kanpur.
October 1986.

CERTIFICATE

Certified that the work "Sulfur Mediated Induced Electron Transfer Reactions in the Chemistry of Thiotungstates," presented in this thesis has been carried out by Mr. Mohd. Asim Ansari, under my supervision and the same has not been submitted elsewhere for a degree.



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CERTIFICATE OF COURSE WORK

This is to certify that Mr. Mohd. Asim Ansari has satisfactorily completed all the courses required for the Ph.D. degree program. The courses include:

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Chm 524 Modern Physical Methods in Chemistry
Chm 525 Principles of Physical Chemistry
Chm 545 Principles of Inorganic Chemistry
Chm 581 Basic Biological Chemistry
Chm 646 Bio-Inorganic Chemistry
Chm 800 General Seminar
Chm 801 Special Seminar
Chm 900 Post-Graduate Research

Mr. Mohd. Asim Ansari was admitted to the candidacy of the Ph.D. degree in September 1984 after he successfully completed the written and oral qualifying examinations.

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I extend my thanks to all the staff members of the department especially to Mr. N. Ahmed for helping me in many ways. I thank Mr. R.D. Singh for the excellent typing of my thesis.

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Mohd. Asim Ansari

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SYNOPSIS

The thesis entitled, 'Sulfur Mediated Induced Electron Transfer Reactions in the Chemistry of Thiotungstates,' consists of four chapters.

Chapter 1 describes a general account of induced intramolecular redox processes citing the first example of this type of reaction from cobalt chemistry and its development to understand similar reactions involved across M=S bond in the chemistry of Mo and W.

Conversion of sulfido to persulfido group and vice versa involving intramolecular electron transfer using external inducing agents have been correlated with biological systems. A brief survey of molybdenum-sulfur and tungsten-sulfur compounds has been presented.

Chapter 2 deals with the scope of the present work. Various possible modes to invoke induced electron transfer across W=S bond have been discussed. When chemical stimuli have been proposed to bring about such reactions, variation of the inducing source and the suitable changes in the reaction conditions, have been stressed upon. An approach to exploit the utility of induced electron transfer reactions as synthetic strategy to obtain hitherto inaccessible compounds of tungsten is outlined.

Chapter 3 describes the experimental procedures and the details involved in the present work. This chapter has been

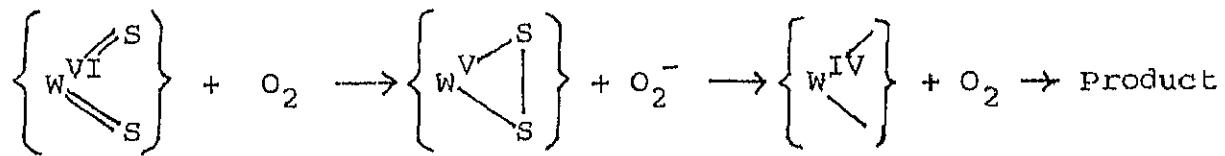
divided into five parts. Chapter 3.1 gives an account of the work-up manipulations of the synthesized compounds and the methods used to analyze them. Part 3.2 describes the methods of the preparations of the starting materials used. Part 3.3 presents induced electron transfer reactions brought about by chemical means. Reaction of $W^{VI}OS_3^{2-}$ with one or two electron oxidant yields a dinuclear species $[W_2^{V}O_2(\mu-S)_2(S_2)_2]^{2-}$. However, when $W^{VI}S_4^{2-}$ is used as the reactant, the known trinuclear cluster $[W^{IV}S(W^{VI}S_4)_2]^{2-}$ or $[W^{IV}O(W^{VI}S_4)_2]^{2-}$ is formed depending upon the reaction conditions. When $[W_2^{V}O_2(\mu-S)_2(S_2)_2]^{2-}$ is treated with polysulfide solution it reverts back to $W^{VI}OS_3^{2-}$, where polysulfide functions as an external reductant. The anion $[W_2^{V}O_2(\mu-S)_2(S_2)_2]^{2-}$ reacts readily with activated acetylene to give dithiobutene complex anion, $[W_2^{V}O_2(\mu-S)_2(S_2C_2R_2)_2]^{2-}$ ($R = COOMe, COPh$). Reaction of $W^{VI}S_4^{2-}$ with activated acetylene gives trisdithiobutene complex anion, $[W^{IV}(S_2C_2R_2)_3]^{2-}$. Reaction of $[W_2^{V}O_2(\mu-S)_2(S_2)_2]^{2-}$ and excess CN^- produces $[W_2^{V}O_2(\mu-S)_2(CN)_6]^{4-}$ anion. Part 3.4 deals with the synthesis of the compounds which apparently seem to be formed by ligand based redox processes. Reaction of dialkylaminium salts of oxotriithiotungstate and tetrathiotungstate with excess CS_2 in the presence of air, at room temperature gives heptacoordinated air stable persulfido complexes, $[W^{VI}O(S_2)(S_2CNR_2)_2]$ and $[W^{VI}S(S_2)(S_2CNR_2)_2]$, respectively. However, treatment of $(R_2NH_2)_2W^{VI}S_4$ with controlled amount of CS_2 yields the anionic compound, $(R_2NH_2)[W^{VI}O(S_2)_2(S_2CNR_2)]$. The neutral complexes, $[W^{VI}O(S_2)(S_2CNR_2)_2]$ and $[W^{VI}S(S_2)(S_2CNR_2)_2]$ when reacted with

KCN undergo reductive elimination yielding $[\text{W}^{\text{V}}\text{O}(\text{S}_2\text{CNR}_2)_2]$. This coordinatively unsaturated complex reacts with elemental sulfur in an oxidative addition fashion, reverting back to $[\text{W}^{\text{VI}}\text{O}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2]$. Part 3.5 covers thermally induced electron transfer reactions. Reaction of $(\text{R}_2\text{NH}_2)_2\text{W}^{\text{VI}}\text{OS}_3$ and $(\text{R}_2\text{NH}_2)_2\text{W}^{\text{VI}}\text{S}_4$ with CS_2 under reflux condition results in the formation of dinuclear neutral complexes $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNR}_2)_2]$ and $[\text{W}_2^{\text{V}}\text{S}_2(\mu\text{-S})_2(\text{S}_2\text{CNR}_2)_2]$ respectively. The same products are obtained when $(\text{NH}_4)_2\text{W}^{\text{VI}}\text{O}_2\text{S}_2$ and $(\text{NH}_4)_2\text{W}^{\text{VI}}\text{S}_4$ are treated with tetraalkylthiuram disulfide at high temperature. Mononuclear complexes, $[\text{W}^{\text{VI}}\text{O}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2]$ and $[\text{W}^{\text{VI}}\text{O}(\text{S}_2)_2(\text{S}_2\text{CNR}_2)]^2-$ undergo disproportionation, by thermal means, yielding the dinuclear compound $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNR}_2)_2]$. $[\text{W}_2^{\text{V}}\text{OS}(\mu\text{-S})_2(\text{S}_2\text{CNR}_2)_2]$ reacts with KCN to give $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNR}_2)_2]$.

First part of the Chapter 4 presents, the strategies involved in the synthesis of the complexes mentioned above, in terms of intramolecular electron transfer reactions. Synthesis of $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ from $\text{W}^{\text{VI}}\text{OS}_3^{2-}$ involves the conversion of four sulfido groups to two persulfido groups and sharing of the electrons released by internal oxidant, W(VI) and external oxidant, I_2 , $\text{S}_2\text{O}_8^{2-}$, ROOR or RSSR, equally. In case of WS_4^{2-} , two electron reduction takes place at the same metal center, yielding trinuclear cluster $[\text{W}^{\text{IV}}\text{S}(\text{W}^{\text{VI}}\text{S}_4)_2]^{2-}$ or $[\text{W}^{\text{IV}}\text{O}(\text{W}^{\text{VI}}\text{S}_4)_2]^{2-}$ depending upon the reaction conditions.

In the complimentary reaction, the conversion of $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ to $2\text{W}^{\text{VI}}\text{OS}_3^{2-}$ using S_x^{2-} as an external reductant leads metal to ligand electron transfer. Conversion of two

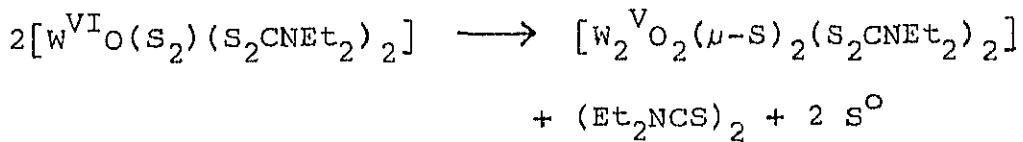
persulfido to four sulfido groups requires four electrons which are supplied by internal reductant $W(V)$ and external reductant S_x^{2-} . Reactions of $[W_2^{VII}O_2(\mu-S)_2(S_2)_2]^{2-}$ with activated acetylenes and CN^- yield the products which retain the oxidation state of tungsten of the starting compound. Reaction of $(R_2NH_2)_2WOS_3$ and $(R_2NH_2)_2WS_4$ with excess CS_2 in the presence of air gives the neutral products $[W^{VI}O(S_2)(S_2CNR_2)_2]$ & $[W^{VI}S(S_2)(S_2CNR_2)_2]$ having metal center in the same oxidation state. Involvement of metal center in intramolecular electron transfer process is confirmed, as an ESR active, pentavalent monomeric species is formed during the course of the reaction. On the basis of above observation, the following scheme has been proposed:



The generation of superoxide radical ion has been verified by specific chemical reactions.

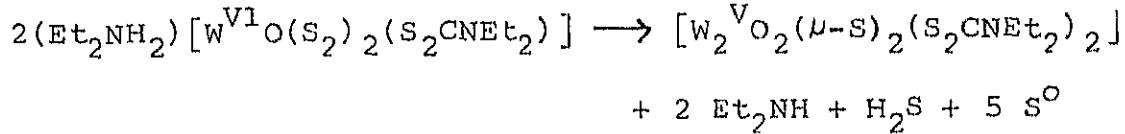
Formation of $(R_2NH_2)[W^{VI}O(S_2)_2(S_2CNR_2)]$ when limited amount of CS_2 is used shows that the formation of dithiocarbamate in the synthesis of $[W^{VI}O(S_2)(S_2CNR_2)_2]$ takes place in steps. However, the same reactants under reflux condition give dinuclear species $[W_2^{VII}O_2(\mu-S)_2(S_2CNR_2)_2]$, $[W_2^{VII}S_2(\mu-S)_2(S_2CNR_2)_2]$ and $[W_2^{VII}OS(\mu-S)_2(S_2CNR_2)_2]$ with reduced metal centers. This series of reactions can best be termed as thermally induced electron transfer reactions.

Thermal induction of $[\text{W}^{\text{VI}}\text{O}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$ results in ligand \rightarrow metal electron transfer and the disproportionation of S_2^{2-} ligand as shown below:

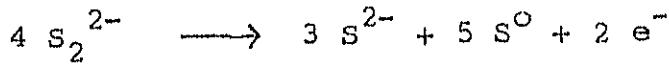


Formation of elemental sulfur could be accounted for through thermal cleavage of S_2^{2-} to S^{2-} and S^{O} .

In the case of $(\text{Et}_2\text{NH}_2)[\text{W}^{\text{VI}}\text{O}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)]$, S_2^{2-} ligands do not cleave simply to produce S^{2-} and S^{O} but also induce the reduction of W(VI) to yield W(V) dimer:



Or precisely the disproportionation reaction is as follows:



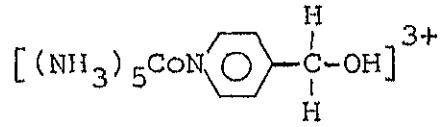
Second part of Chapter 4 describes the physico-chemical and structural investigations of the synthesized compounds described in the preceding chapter. The studies include IR, electronic, ^1H NMR, ^{13}C NMR and ESR spectroscopy; C.V. and X-ray crystal structure.

Chapter 1

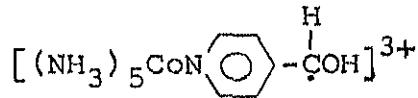
INTRODUCTION

Electron transfer reactions involving outer-sphere mechanism and inner-sphere mechanism are well documented in the literature. Pioneering work, in this area has been done by Taube and co-workers.¹⁻⁶ In the early sixties of this century, the same school discovered another class of reactions which involves intramolecular electron transfer under the influence of some external agent.⁶ This class of reactions was given the name, "Induced Electron Transfer Reactions." Electron transfer can be induced by several kind of operations on the ligand. It can be achieved either by chemical means or by physical stimuli. The reactions of this type were first studied in cobalt chemistry. For a better understanding of the nature of this type of reactions, the essence of this process is briefly outlined below.

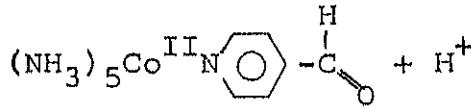
Consider the complex ion



which contains the one-electron oxidizing center Co(III) and a function, the carbinol group, which requires a two electron oxidant for stable product to be formed. Though the metal is in the oxidized state and the carbinol function of the attached ligand is in the reduced state, the intramolecular electron transfer between these two redox active centers is extremely slow because the Co(III) anion complex is a sluggish oxidant to function on a two electron reducing group like carbinol. For the oxidation of the carbinol function, oxidizing agent like Ce(IV), Mn(III) or $[\text{Co(III)aq.}]$ having E° value in the range of 1.5 V is required. The essence of induced electron transfer reaction lies in the fact that the external oxidants having high E° value are not able to affect the Co(III) center present in the complex directly. They can attack the oxidizable carbinol function with the generation of some reactive species carrying an odd electron, most probably in the form of an organic radical. Thus, under the influence of external oxidant, a reactive intermediate species of the complex can be formed like



With the presence of this odd electron the internal electron transfer may take place to produce



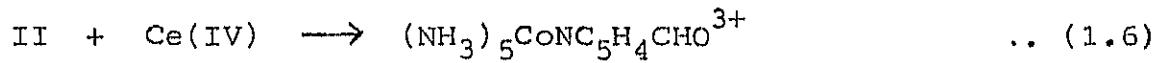
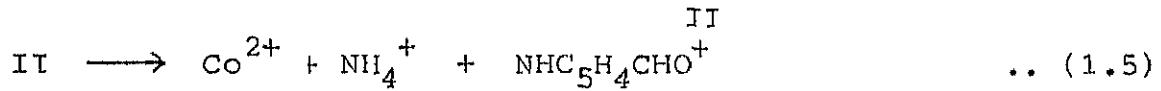
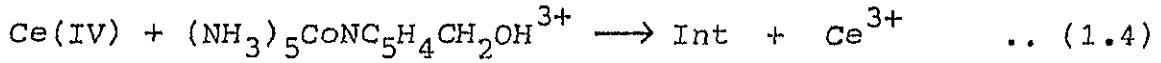
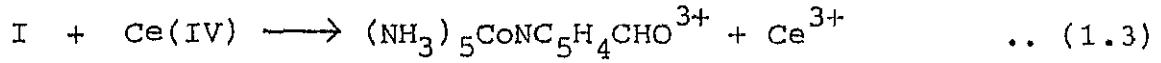
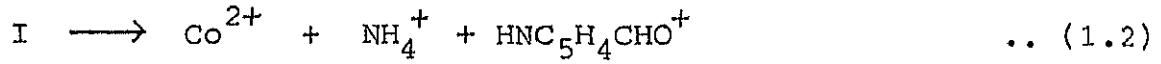
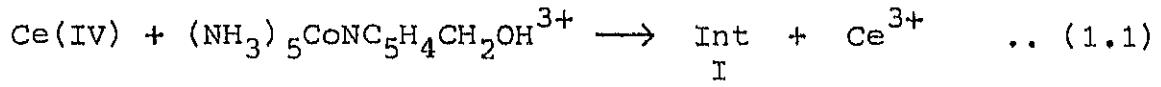
The overall reaction is novel in the sense that under the influence of one electron oxidant as an external source, Co(III) in the complex (internal oxidant) gets reduced at the expense of sharing one electron donated by the carbinol function which changes to aldehyde function. As the generated Co(II) species is very labile to substitution, the complex can dissociate to give Co(II), NH_4^+ and $[\text{HN} \begin{array}{c} \text{H} \\ \text{C}_6\text{H}_4 \end{array} - \text{C}=\text{O}]^+$ in acidic solution. The mode of action of the external oxidant in the present case is to initiate one electron change. The other possibility might exist where the two electron change occurs without formation of a radical or the reduction of internal oxidant (Co(III)).⁷

A direct two electron participation between the external oxidant and the ligand center is then a purely ligand based redox reaction. For induced electron transfer reaction, it is essential to prove that the reduced form of the internal oxidant is among the products of the reaction. Cobalt chemistry is unique in this sense as Co(II) complexes thus formed by induced electron transfer are by large, substitution labile and identification of Co(II) in the reaction medium specially in acidic medium is an easy task. The corresponding Ru(II) system is much less labile than Co(II) and the stability of the reduced intermediate might cause reoxidation by the external oxidant to produce Ru(III) species as the product.⁸ Situation of this type might cause difficulties in differentiating the nature of electron transfer reaction between induced electron transfer and purely a ligand based redox reaction.⁹

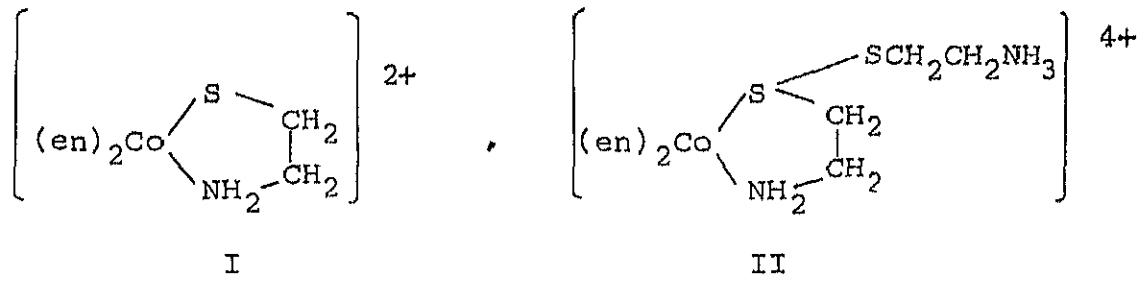
A very important question regarding induced electron transfer reaction is whether the external and internal oxidants function in concerted manner or the external oxidant acts first to produce reaction intermediate which in turn participates in intramolecular electron transfer. Candlin and Halpern⁹ provided the first kinetic data to establish that the internal electron-transfer takes place after the external oxidant has played its role. In some of the reactions using Co(III) complex, when attacked by specific external oxidant say $\text{Cr}_2\text{O}_7^{2-}$ no radical intermediate is formed and the reaction is a simple ligand based two electron exchange reaction.¹⁰

The possibility of these two alternative mechanisms i.e., induced electron transfer and ligand based electron transfer reaction taking place in a single reaction has been explored by using a catalyst along with the external oxidant. Thus, Ce(IV) when allowed to function as an external oxidant in the presence of Ag^+ with the 4-pyridinemethanol-cobalt(III) system shows the formation of two intermediates. Kinetic data establish that both the intermediates can undergo internal electron transfer reaction. However, one intermediate undergoes internal electron transfer uninterrupted by the presence of the external oxidant while the other intermediate lives sufficiently long to undergo oxidation by external oxidant in competition with the internal electron transfer reaction. It is clear that two intermediates are formed by parallel events which conclude the following mechanism to

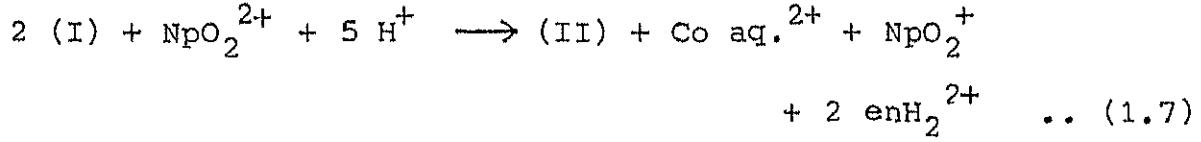
account for the results: ¹¹⁻¹⁴



Till early seventies, studies on such reactions were done mainly from the point of view of kinetics. The subject took a new dimension when this methodology was exploited as a strategy to achieve some difficult synthetic goal. In 1975 Deutsch and co-workers reported the synthesis of the first cobalt(III) disulfide complex invoking induced electron transfer process. ¹⁵



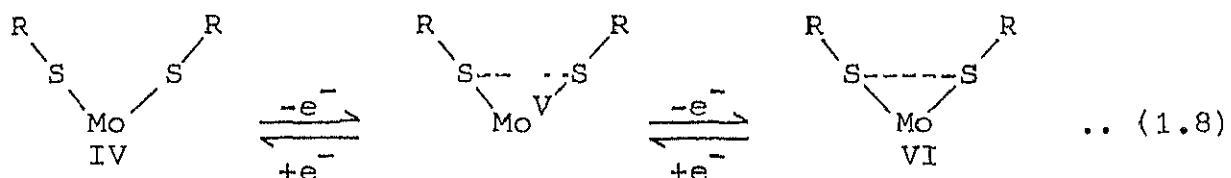
Compound (I) is oxidized by Np^{VI} as:



(II) results from (I) by a two electron oxidation, one arising from Np^{VI} and the other arising from a molecule of (I) which in turn is converted to $[\text{Co}_{\text{aq.}}]^{2+}$. Since most of the metalloenzymes contain sulfur either in the form of sulfide or coordinated thiol, this mode of metal-thiol interaction is relevant to biological systems which contain the $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ and $\text{Cu}^{\text{I}}\text{-Cu}^{\text{II}}$ couples. Subsequently Taube and co-workers¹⁶ exploited this methodology to synthesize disulfide complexes of ruthenium which were not accessible earlier by any other conventional methods.

Thus the exploitation of this chemistry of electron transfer reactions has many facets namely, synthesis of newer complexes which are not accessible by using conventional redox or other reactions and an understanding of the change occurring in the coordinated ligand center along with the participation of the central metal atom. Generally sulfur containing metalloenzymes have sulfur in the form of coordinated thiol groups or as labile inorganic sulfides. Dithiol-disulfide redox centers are present even in many metal free enzymes such as in the stable thioredoxin which forms a hydrogen transferring system with thioredoxin reductase.¹⁷ In xanthine oxidase a persulfido ligand may play a key role in its enzymatic turn over. The ready conversion of molybdenum center from +VI to +IV via +V takes place with the loss of a terminal sulfido group in the oxidation process of the substrates. EXAFS studies¹⁸⁻²⁰ indicate that the conversion of sulfido group to thiol group results in elongation of the Mo-S bond. Stiefel and co-workers^{21,22} correlated the spectroscopic

redox and catalytic properties of the enzyme assuming SR^- functions as ligand (vide infra):



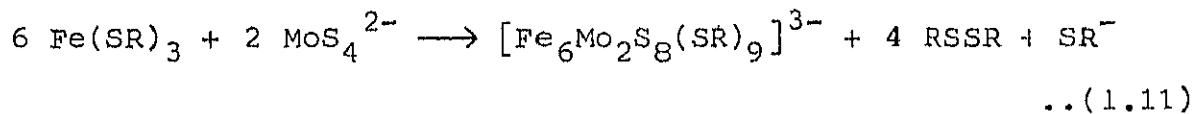
It is inferred that the *cis* position of molybdenum bound thiolate can change to a triatomic unit comprising of $\{\text{MoS}_2\}$ core with different degrees of S-S bond formation depending on the redox state of the molybdenum center. The regeneration stage of the enzyme under aerobic conditions involves stepwise oxidation with the intermediate formation of O_2^- which is a complimentary set of reaction in a reverse manner.²³ Thiomolybdate reactions (1.8) and (1.10) shown below are complimentary to each other.^{24,25}



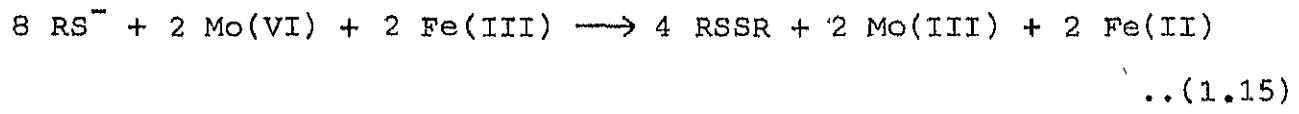
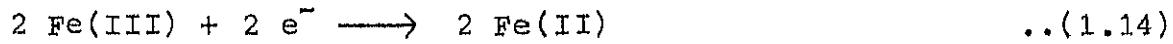
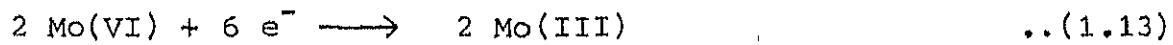
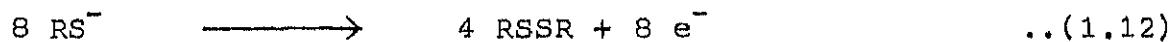
The high yield reactions of the above type are illustrated examples of a novel chemistry of molybdenum sulfur systems where a Mo=S group can be effectively converted into Mo-(S_2) group and vice-versa. The process involves the change in oxidation state of molybdenum from VI to IV. Reaction (1.9) is a good example of induced electron transfer reaction where elemental sulfur functions as an external oxidant and Mo(VI) in MoS_4^{2-} acts as

an internal oxidant. Here coordinated sulfido group releases the necessary electrons for the reaction. The complimentary reaction involves dithiol as an external reductant and Mo(IV) in MoS_9^{2-} as internal reductant with the reduction of coordinated S_4^{2-} ligands to S^{2-} ligands. In biological processes the involvement of such redox reactions may be triggered by physical or chemical stimuli. For induced electron transfer reactions similar stimulations have already been observed. Metalloenzymes normally function in conjunction with many electron carrier proteins involving several prosthetic groups. In xanthine oxidase the molybdenum cofactor operates with flavin and iron sulfur proteins. Bray and co-workers²⁶ have shown that the electron transfer reaction from the substrate to the molybdenum center of the enzyme is a concerted process. This suggests that the flavin and iron sulfur prosthetic group of the enzyme function concomitantly with molybdenum cofactor, the binding site of the substrate of the enzyme. When xanthine dehydrogenase functions the flavin part is not in operation. Interestingly for its regeneration an one electron oxidant is necessary. The involvement of flavin in the regeneration stage of xanthine oxidase by two electron oxidant oxygen, suggests the sharing of the reduction process by both flavin as well as molybdenum center of the enzyme. Though in principle, molybdenum in its reduced state i.e. IV can affect the reduction of oxygen by two electrons, yet the involvement of flavin to share this redox process is reminiscent of an induction process where oxygen might play the role of an external oxidant,

which induces the electron transfer via flavin to molybdenum sulfur bond. The hydroxylation of xanthine to uric acid incorporates oxygen from water, and not from the air.²⁶ It suggests that the role of oxygen in the regeneration stage of this enzyme is simply to activate flavin which might induce the electron transfer across Mo-SR bond with the formation of Mo=S bond in the oxidized form of the enzyme. Several interesting reactions in metal sulfur chemistry can be exemplified in terms of induced electron transfer reactions. Thus the formation of the double cubane cluster comprised of iron-molybdenum and sulfur is a nice example in this regard.^{27,28}



In the above reaction iron is as Fe(III) and molybdenum is as Mo(VI) in the reactants which give the double cubane. It has been found that four of the iron centers are as Fe(III) and two as Fe(II) and molybdenum centers are as Mo(III) in the double cubane. The above reaction may be viewed as induced electron transfer process as follows:



Here MoS_4^{2-} functions as an external oxidant which induces electron transfer from coordinated SR^- to Fe(III) which represents the internal oxidant in this process. The electrons donated by SR^- during its oxidation to RSSR are shared by Mo(VI) and Fe(III) to form the double cubane. All the reactants after this type of electron transfer, rearrange to have a thermodynamically stable heterometallic aggregate. Physical and chemical stimulation of thiomolybdates and thiotungstates result in the induction of intramolecular redox reactions across M-S (M = Mo, W) bond. The use of this type of chemistry as synthetic strategy to isolate and characterize newer compounds is a recent phenomenon. This chemistry is not restricted to aqueous medium only. Some interesting results have been obtained using aprotic solvents and even in the solid state.³¹ Table 1.1 gives representative examples of intramolecular induced redox reactions involved in the isolation of newer species.

A detailed energy level calculation on $[\text{Mo}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$ ²⁹ implies that the frontier orbitals of the systems are predominantly Mo and S in character and lie very close in energy. Systems of this type are most suitable to study thermal or photochemical activation to induce internal redox reaction. Participation of a ligand involving these types of excitation processes has been predicted long back by Taube and co-workers.¹⁰ In fact it has been observed recently that the conversion of $(\text{NH}_4)_2\text{MoS}_4$ to MoS_3 upon heating involves metal reduction and ligand oxidation.^{30,31} A photochemical induction using visible light has been recently

reported.³² This involves the conversion of a Mo(V) sulfido complexes ($\text{Cp}_2\text{Mo}_2\text{S}_4$) to an Mo(IV) disulfido complex $[(\text{Cp}_2\text{Mo}_2\text{S}_2)(\text{S}_2)]$. The involvement of aerial oxygen as an external oxidant to convert MoS_4^{2-} to $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ at room temperature is an example of the participation of $\text{S} \rightarrow \text{Mo}$ redox by chemical means.³³ The chemical stimulation of thiomolybdates has been studied using different external oxidants like oxygen, elemental sulfur and organic disulfide. In all these cases the basic reaction is the reduction of molybdenum with the oxidation of the sulfide ligands.³²⁻³⁵

The chemistry of heterothiomolybdates is very similar to that of heterothiotungstates with a few exceptions i.e. say when the other heterometal is iron. However, a careful examination of these two systems show similarity in reactivity sometimes. The only difference lies in the more facile reactivity of molybdenum systems compared to that of tungsten systems. Isolation of $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ ^{50,51} compared to $[\text{Fe}(\text{WS}_4)_2]^{2-}$ may be taken as an illustrated example of this behaviour. However, $[\text{Fe}(\text{WS}_4)_2]^{2-}$ does give $[\text{Fe}(\text{WS}_4)_2]^{3-}$ under reducing condition and even on long standing in solution wherein the corresponding molybdenum analog is formed more readily even without addition of any external reducing agent.^{52,53} No clear explanation for this difference in reactivity may be furnished in some simple norms because the celebrated double cubane clusters comprising of $\{\text{Fe}_6\text{W}_2\}$ core is formed in almost identical conditions to its molybdenum analog.⁵⁴ A recent report of molybdenum-iron-sulfur cluster

formation of the type $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}_2)_2(\text{S-p-C}_6\text{H}_4\text{Br})_6]^{4-}$ shows that corresponding tungsten analog can not be synthesized under similar conditions, clearly indicating difference in reactivity.⁵⁵

The difference between molybdenum-sulfur and tungsten sulfur systems is wide, when the formation of homometallic cluster compounds are considered. Polythiomolybdates are formed readily using different methodologies. Some representative polythiomolybdates are presented in Table 1.2. The corresponding polythiotungsten compounds are by large yet not known and even if some of them are known, the synthetic strategies are entirely different. Interestingly, the isolation of $\text{W}_4\text{S}_{12}^{2-}$ and $\text{W}_3\text{S}_8^{2-}$ has no resemblance in molybdenum systems so far.^{44,45} The sluggishness of tungsten sulfur systems may be due to larger separation in energy of the frontier orbitals which are predominantly W and S in character. However, in some cases it can be overcome invoking this newer methodology, induced electron transfer process, as shown in Table 1.1.

Reactions

The reactivity of sulfido and polysulfido compounds of molybdenum and tungsten are varied in nature and the general pattern of these reactions can be described as follows:

Table 1.1 Representative Examples of Induced Electron Transfer Reactions Across M-S bond (M = Mo, W)

Starting Material	Reaction Medium	Inducing Agent	Product	Reference
1	2	3	4	5
$\text{MoO}_2\text{S}_2^{2-}$	$\text{KOH}/\text{H}_2\text{S}/\text{H}_2\text{O}$	Thermal, O_2	$[\text{Mo}_2\text{V}\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$	36
MoS_4^{2-}	$\text{S}_x^{2-}/\text{H}_2\text{O}$	Thermal	$[\text{Mo}_3^{\text{IV}}\text{S}(\text{S}_2)_6]^{2-}$	37
MoS_4^{2-}	$\text{S}_x^{2-}/\text{H}_2\text{O}$	Thermal	$[\text{Mo}_2\text{V}(\text{S}_2)_6]^{2-}$	38
MoS_4^{2-}	DMF	Thermal	$[\text{Mo}_2\text{V}\text{S}_2(\mu-\text{S})_2(\text{S}_2)(\text{S}_4)]^{2-}$	34
MoS_4^{2-}	DMF	O_2	$[\text{Mo}_2\text{V}\text{O}_2(\mu-\text{S})_2(\text{S}_2)(\text{S}_3\text{O}_2)]^{2-}$	39
MoS_4^{2-}	CH_3CN	S	$[\text{Mo}^{\text{IV}}\text{S}(\text{S}_4)_2]^{2-}$	24
$(\text{NH}_4)_2\text{MoS}_4$	Solid State	Thermal	$[\text{Mo}_2\text{V}(\text{S}_2)(\text{S}_4)]$	31
$(\text{Cp})_2\text{Mo}_2\text{V}\text{S}_4$		Photochemical (visible)	$[(\text{Cp})_2\text{Mo}_2^{\text{IV}}\text{S}_2(\text{S}_2)]$	32
MoS_4^{2-}	DMF	Thermal	$[\text{Mo}^{\text{IV}}\text{S}\text{Mo}^{\text{VI}}(\text{S}_4)_2]^{2-}$	40
MoS_4^{2-}	$\text{CH}_3\text{CN}/\text{DMF}$	Dithiol	$\text{Mo}^{\text{VI}}\text{S}_4^{2-}$	25
MoS_9^{2-}	DMF	$(\text{PhS})_2$	$[\text{Mo}_2^{\text{V}}\text{S}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$	25
MoS_4^{2-}	H_2O	$\text{O}_2, \text{H}^+(\text{H}_2\text{SO}_4)$	$[\text{Mo}_2^{\text{V}}\text{OS}(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$	41
MoS_4^{2-}	CH_3CN	Tetraethyl-thiuram disulfide	$[\text{Mo}^{\text{V}}\text{S}_2(\text{X}\text{S}_2\text{CNEt}_2)_3]$	42
WS_4^{2-}	H_2O	H^+	$[\text{W}^{\text{IV}}\text{O}(\text{W}^{\text{VI}}\text{S}_4)_2]^{2-}$	43

... contd.

Table 1.1 (contd.)

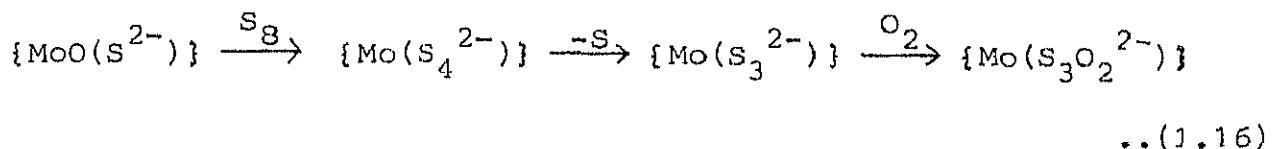
1	2	3	4	5
WS_4^{2-}	MeOH	H^+	$[W^{IV}S(W^{VI}S_4)_2]^{2-}$	40
WS_4^{2-}	CH_2Cl_2	H^+	$[W^{II}(W^{VI}S_4)_2]^{2-}$	44
WS_4^{2-}	DMF	1,2-Ethane dithiol	$[W_2^VS_2(\mu-S)_2(W^{VI}S_4)_4]^{2-}$	45, 46
WS_4^{2-}	DMF	S	$[W_2^VS_2(\mu-S)_2(edt)_2]^{2-}$	47
WS_4^{2-}	DMF	Thermal, coordi- nated S^{2-}	$[W^{IV}S(W^{VI}S_4)_2]^{2-}$	48, 49
WS_4^{2-}	DMF			40

Table 1.2 Different Types of Polythiomolybdates

Type	Source of sulfur	Starting Material	Product	Reference
$\{\text{Mo}_2\text{S}_2\}^{2+}$	Starting material	$\text{MoO}_2\text{S}_2^{2-}$	$[\text{Mo}_2\text{V}\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$	36
"	"	MoS_4^{2-}	$[\text{Mo}_2\text{V}\text{OS}(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$	42
"	"	MoS_4^{2-}	$[\text{Mo}_2\text{V}\text{S}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$	25
"	Starting material and RSSSR	MoS_4^{2-}	$[\text{Mo}_2\text{V}\text{S}_2(\mu-\text{S})_2(\text{S}_4)_2]^{2-}$	39
"	"	MoS_4^{2-}	$[\text{Mo}_2\text{V}\text{S}_2(\mu-\text{S})_2(\text{S}_2)(\text{S}_4)]^{2-}$	39
"	Starting material	MoOS_3^{2-}	$[\text{Mo}_2\text{V}\text{O}_2(\mu-\text{S})_2(\text{S}_2)(\text{S}_3\text{O}_2)]^{2-}$	40
$\{\text{Mo}_3\text{S}_4\}^{4+}$	Polysulfide	MoO_4^{2-} or MoS_4^{2-}	$[\text{Mo}_3\text{IV}\text{S}(\text{S}_2)_6]^{2-}$	37, 56, 57
"	Starting material	$[\text{Mo}_3(\text{S}_2)_6]^{2-}$	$[\text{Mo}_3\text{IV}\text{S}_4(\text{CN})_9]^{5-}$	58
$\{\text{Mo}=\text{C}_t\}^{2+}$	Elemental sulfur	MoOS_3^{2-}	$[\text{Mo}^{\text{IV}}\text{O}(\text{S}_4)_2]^{2-}$	34
"	Starting material	MoOS_3^{2-}	$[\text{Mo}^{\text{IV}}\text{C}(\text{Mo}^{\text{VI}}\text{S}_4)_2]^{2-}$	43, 59
$\{\text{Mo}=\text{S}_t\}^{2+}$	Starting material and elemental sulfur or RSSSR	MoS_4^{2-}	$[\text{Mo}^{\text{IV}}\text{S}(\text{S}_4)_2]^{2-}$	24
"	Starting material	MoS_4^{2-}	$[\text{Mo}^{\text{IV}}\text{S}(\text{Mo}^{\text{VI}}\text{S}_4)]^{2-}$	41
$\{\text{MoS}_2\text{Mo}\}^{8+}$	Polysulfide	MoO_4^{2-} or MoS_4^{2-}	$[\text{Mo}_2\text{V}(\text{S}_2)_6]^{2-}$	38, 60

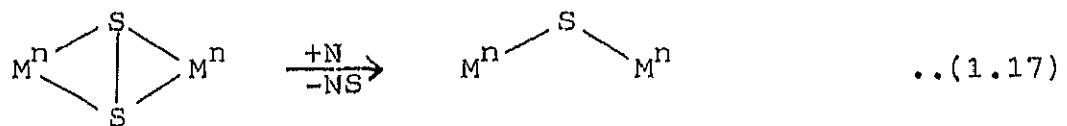
(i) Oxidation of the ligand by external agents

The synthesis of the complex containing $S_3O_2^{2-}$ ligand $[Mo_2O_2(\mu-S)_2(S_2)(S_3O_2)]^{2-}$ from $MoOS_3^{2-}$ and elemental sulfur in the presence of air proceeds according to Scheme (1.16)⁶¹ involving the oxidation of the coordinated S_3^{2-} ligand

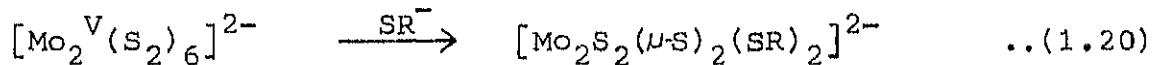
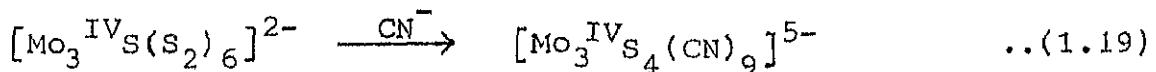
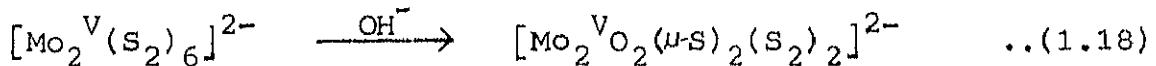


(ii) Reaction with nucleophiles

Abstraction of sulfur atom by nucleophiles (N) such as PPh_3 , SO_3^{2-} , SR^- , CN^- and OH^- is the characteristic feature of disulfido and polysulfido complexes. In disulfido complexes abstraction of sulfur atom takes place in the following way:⁶²⁻⁶⁸

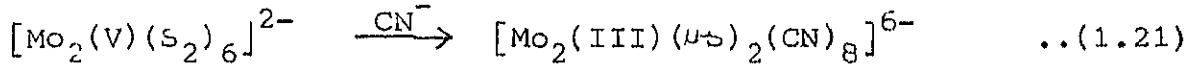


Few representative examples are shown below:



All these reactions involve loss of a neutral sulfur atom from the complex without leading to any change in the formal oxidation state

of the metal atom. These reactions result in the substantial transfer of electron density from the ligand to the metal so that the population of the ligand π^* level is decreased.⁶²⁻⁷⁰ However, reduction of molybdenum center does occur in certain cases when a strong nucleophile like CN^- is used:⁶⁶

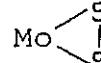


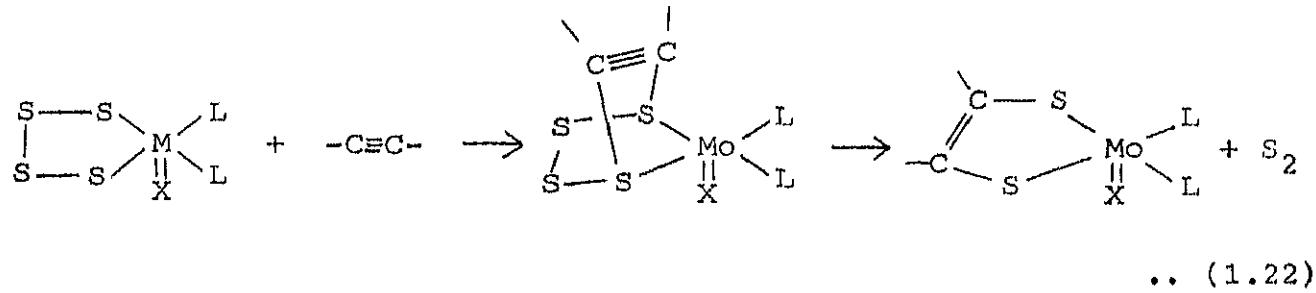
Insertion Reaction

Insertion reactions are of two types i.e. with CS_2 and activated acetylene. Thus MoS_9^{2-} reacts readily with CS_2 with the formation of $[\text{MoS}(\text{CS}_4)_2]^{2-}$ anion. Crystal structure analysis has shown that this anion exists in cis as well as trans configuration.^{71,72} The reaction of $[\text{Mo}_2\text{S}_2(\mu\text{S})_2(\text{S}_2)(\text{S}_4)]^{2-}$ with CS_2 leads to the formation of $[\text{Mo}_2\text{S}_4(\text{CS}_4)_2]^{2-}$ anion.⁷¹ The easy formation of CS_4^{2-} ligand from S_4^{2-} is brought about by dissociation of S_4^{2-} to S_2^{\bullet} followed by interaction with electrophilic molecule CS_2 . The formation of perthiocarbonate ligand with CS_2 is well documented with many other metal polysulfido complexes.⁷³⁻⁷⁵ The reaction of these complexes with electrophile like 2-butynedimethanoate (DMA) is highly interesting. Thus when MoS_9^{2-} reacts with DMA, the trisdithiolene complex $[\text{Mo}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_3]^{2-}$ anion is formed. However, reaction with MoO_8^{2-} produces the penta-coordinate complex $[\text{MoO}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_2]^{2-}$ anion.^{76,77} The formation of dithiolene type of ligand in the reaction of these complexes with DMA differs from the reaction of this activated acetylene with

$[\text{Mo}_2\text{O}_2\text{S}_6]^{2-}$ anions.⁷⁸ Here insertion of DMA takes place into the Mo-S bond rather than S-S bond with the formation of S-C-coordinated vinyl disulfide ligand. It has been observed that the complex anion $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)(\text{S}_4)]^{2-}$ reacts with DMA at ambient temperature to give the same vinyl disulfide complex. Under refluxing conditions, the reaction affords the dithiolene isomer.⁷⁹ It has been proposed that coordinated S_4^{2-} ligand dissociates to S_2^{2-} and S_2° in solution to react rapidly with DMA to form the vinyl disulfide complex which thermally rearranges to the dithiolene isomer. An apparent difference in reactivity between S_2^{2-} and S_4^{2-} ligand has been noticed. X-ray structural data shows that the S-S bond length in this side on bound S_2^{2-} ligand ranges from 2.03 to 2.074 Å and is slightly longer than S-S bond in elemental sulfur S_8 . In contrast in the complex containing S_4^{2-} unit, for example, MoS_9^{2-} where S_4^{2-} acts as a bidentate ligand, the S-S bond directly adjacent to Mo atom elongates which can be correlated with the shortening of the corresponding Mo-S bond. This suggests that bonding electron from the S-S bond are transferred to Mo-S bonding orbitals.

The S-S bond length for the uncoordinated S_2° , S_2^{2-} and S_2^{2-} are 1.89 Å, 2.00 Å and 2.3 Å, respectively. These data together with the S-S bond length observed in several side on coordinated S_2^{2-} species suggest a bond order 1 for the coordinated S_2^{2-} ligand. This strengthening of bond order would originate by the transfer of electron density from the antibonding π^* orbital to the Mo-S bond. This would result in a net depopulation of the

S_2^{2-} orbitals in these complexes.⁸⁰ Furthermore, the π^* nature of LUMO suggests that a cycloaddition of acetylene to the Mo side on bound S_2^{2-} would be a symmetry forbidden process. Hence this cycloaddition reaction of activated acetylene with pure Mo  units are unknown. The only well documented reaction of DMA with such unit in $[Mo_2O_2(\mu-S)_2(S_2)_2]^{2-}$ complex ion⁷⁸ is known in which the alkyne has inserted into Mo-S bond. The formation of dithiolene ligand by the reaction of polysulfido complexes with activated acetylenes are known.⁷⁵ The most likely mechanism is shown below which involves the cycloaddition of the electrophilic alkyne to the coordinated S_x^{2-} chelate.



Scheme 1.1 Cycloaddition of alkyne to the Mo-S unit

Other Reactions

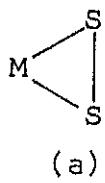
Reductive elimination reactions are also well known. For example, $Cs_2[Mo_2^V(S_2)_6]$ thermally responds to generate S_2 molecule as the main gaseous product with the formation of Mo-S cluster in the lower oxidation state.^{69,81} Thermal decomposition of $(NH_4)_2[Mo_3S(S_2)_6] \cdot nH_2O$ at $270^{\circ}C$ produces one mole of NH_3 and half a mole of H_2S per mole of this trinuclear compound.⁸¹

Physical Studies

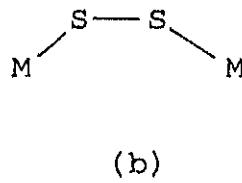
Sulfido and polysulfido complexes of molybdenum and tungsten have been studied extensively using all the conventional physicochemical methods. Whenever complexity arose, X-ray crystal structures were determined. For a few systems effect of temperature has also been studied.^{69,81} There is a trend to study the electrochemical behaviour of such systems. This certainly helps in understanding the mechanistic aspects of metalloenzymes where Mo or W is the active center.^{21,26}

Vibrational Spectra

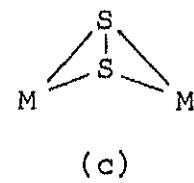
Vibrational spectroscopy has been found to be a very important tool in determining the presence of a particular functional group in such complexes. In most of these cases, it is possible to distinguish among $\nu(S-S)$, $\nu(M-S_t)$ and $\nu(M-S_b)$ group present in the compound. In polysulfido complexes $\nu(S-S)$ frequencies range from ca. 400 to 600 cm^{-1} . Disulfur complexes are broadly classified into three types as shown below:



(a)



(b)



(c)

In all these complexes the $\nu(S-S)$ frequencies range from ca. 480 to 600 cm^{-1} . Comparison of the $\nu(S-S)$ values for the discrete diatomic sulfur species S_2^{3-} ($^3\Sigma_g^-$, 725 cm^{-1}),^{82,83} S_2^{2-} ($^2\text{I}_{1g}$,

589 cm^{-1}), $84, 85 \text{ S}_2^{2-}$ (${}^1\Sigma_g^+$, 446 cm^{-1})⁸⁶ leads to the conclusion that the approximate charge distribution in disulfur complexes is some where between that for S_2^- and that for S_2^{2-} . However, there is a strong coupling of the $\nu(\text{S-S})$ vibration with the $\nu(\text{M-S})$ vibrations leading to higher $\nu(\text{S-S})$ values. This coupling has been confirmed by observing the shift of $1-2 \text{ cm}^{-1}$ in $\nu(\text{S-S})$ upon substitution of ^{92}Mo by ^{100}Mo in $[\text{Mo}_2(\text{S}_2)_6]^{2-}$ and $[\text{Mo}_3\text{S}(\text{S}_2)_6]^{2-}$.⁸⁷⁻⁸⁹

The $\nu(\text{M-S}_n)$ vibrations are generally observed in the range 250 to 420 cm^{-1} . The $\nu(\text{M-S}_t)$ and $\nu(\text{M-S}_b)$ are observed in the range 480 to 550 cm^{-1} and 430 to 460 cm^{-1} , respectively.⁹⁰⁻⁹³ The typical examples are presented in Table 1.3.

Electronic Spectra

Study of the electronic spectra of sulfido and polysulfido complexes of molybdenum and tungsten shows that most of the bands in the low energy region are due to charge transfer either from ligand to metal or metal to ligand. The longest wavelength band in the complexes like $[\text{MoO}(\text{S}_2)(\text{S}_2\text{CNEt}_2)_2]$ is assigned to the ligand to metal charge transfer.⁹⁴ This assignment is also correct for other disulfido complexes where metal atoms are in high oxidation state, e.g. $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]$.^{36, 69} Position of the band in this region is influenced by the oxidation state of the metal, metal-metal bond and also the nature of the ligand present. However, these assignments are only tentative and correct assignments are still open to question.

Table 1.3 Infrared Spectral Data

Compound	Frequencies in cm^{-1}						$\nu(\text{M}-\text{O}_{\text{term}})$	Reference
	1	2	3	4	5	6	7	
$\text{Mo}^{\text{VI}}\text{OS}_2(\text{S}_2\text{CNPR}_2)_2$	556	374, 350	—	—	—	916	94	
$\text{CpMo}^{\text{IV}}(\text{S}_2)$	530	386, 351	—	—	—	—	95	
$\text{Mo}^{\text{V}}\text{S}_2(\text{S}_2\text{CN}^{\text{+}}\text{Et}_2)_3$	555	not reported	—	—	—	—	42	
$\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{CN}^{\text{+}}\text{Et}_2)_2$	—	—	—	—	—	910, 877	96	
$\text{Mo}_2^{\text{V}}\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{CN}^{\text{+}}\text{Et}_2)_2$	—	—	—	477, 340	967, 952	97		
$\text{Mo}_2^{\text{V}}\text{OS}(\mu-\text{S})_2(\text{S}_2\text{CN}^{\text{+}}\text{Et}_2)_2$	—	—	544	471, 337	962, 956	97		
$\text{Mo}_2^{\text{V}}\text{S}_2(\mu-\text{S})_2(\text{S}_2\text{CN}^{\text{+}}\text{Et}_2)_2$	—	—	548, 538	463, 334	—	97		
$[\text{Mo}_2^{\text{V}}\text{C}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$	516, 508	357, 321	—	not assigned	925	36		
$[\text{Mo}_2^{\text{V}}\text{S}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$	520	350	535	460	—	25		
$[\text{Mo}_2^{\text{V}}\text{OS}(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$	518	350	not reported	460	940	39		
$[\text{Mo}_2^{\text{V}}(\text{S}_2)_6]^{2-}$	550, 551	382, 361, 354	—	—	—	38		
$[\text{Mo}^{\text{IV}}\text{S}(\text{S}_2)_6]^{2-}$	544	386, 361	—	—	—	37		
$[\text{Mo}^{\text{IV}}\text{S}(\text{MoS}_4)_2]^{2-}$	—	—	527	not assigned	—	40		
$[\text{Mo}^{\text{IV}}\text{O}(\text{S}_4)_2]^{2-}$	not assigned	—	—	—	930	34		

...cont'd.

Table 1.3 (contd.)

1	2	3	4	5	6	7
$[\text{Mo}^{\text{IV}}\text{S}(\text{S}_4)^2]^{2-}$	-	-	525	-	-	24
$[\text{W}_2^{\text{V}}\text{S}_2(\mu-\text{S})_2(\text{S}_4')_2]^{2-}$	-	-	495, 506	-	-	48, 49
$[\text{W}_2^{\text{V}}\text{S}_2(\mu-\text{S})_2(\text{W}^{\text{VI}}\text{S}_4)_2]^{2-}$	-	525	448, 350	-	-	45, 46
$[\text{W}^{\text{IV}}\text{S}(\text{W}^{\text{VI}}\text{S}_4)_2]^{2-}$	-	525, 490, 485	465, 435	-	-	40
$[\text{W}^{\text{IV}}\text{O}(\text{W}^{\text{VI}}\text{S}_4)_2]^{2-}$	-	495	465, 453	970	40, 43	
$[\text{W}^{\text{III}}(\text{W}^{\text{VI}}\text{S}_4)_2]^{2-}$	-	495, 490	465, 453	-	-	44
$[\text{W}^{\text{VI}}\text{S}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	550	-	500	-	-	42

Table 1.4 presents electronic absorption maxima for few representative examples.

X-Ray Studies

A variety of sulfido and polysulfido complexes of group VIB elements are known and there is a continuous addition to this. In certain cases the vibrational spectroscopy and other conventional techniques fail to resolve the complexity of the problem, and X-ray structure determination is the ultimate choice. Structures of most of these complexes have been determined and structure of few representative examples are shown in Figs. 1.1 & 1.2. Bond length of some of these complexes are given in Table 1.5. In most of the complexes bond distances lie in the range expected for sulfur ring. The alteration in the S-S bond lengths have been rationalized in terms of significant $M(d\pi) - S(d\pi)$ interactions which perturb the $S(d\pi) - S(d\pi)$ bonding between central atom.⁹⁸

Table 1.4 Electronic absorption bands

Compounds	Colour	Band maximum (nm)	Reference
$[\text{Mo}^{\text{V}}\text{O}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	Blue	394, 581	94
$[\text{Mo}_2^{\text{V}}\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$	Red orange	278, 305, 370, 463	36
$[\text{Mo}_2^{\text{V}}\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$	Purple	295, 467, 573	25
$[\text{Mo}_2^{\text{V}}(\text{S}_2)_6]^{2-}$	Black green	313, 357, 417, 500, 625, 769	38, 60
$[\text{Mo}_3^{\text{IV}}\text{S}(\text{S}_2)_6]^{2-}$	Red	333, 370, 465, 541	37
$[\text{Mo}^{\text{IV}}\text{O}(\text{S}_4)_2]^{2-}$	Green	316, 475, 555	34
$[\text{Mo}^{\text{IV}}\text{S}(\text{S}_2)_2]^{2-}$	Red	316, 340, 405, 470	34
$[\text{Mo}^{\text{IV}}\text{S}(\text{Mo}^{\text{VI}}\text{S}_4)_2]^{2-}$	Dark red	270, 460	40
$[\text{W}^{\text{VI}}\text{S}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	Green	602, 394, 360	42
$[\text{W}_2^{\text{VI}}\text{S}_2(\mu-\text{S})_2(\text{W}^{\text{VI}}\text{S}_4)_2]^{2-}$	Dark red	385, 294	48, 49
$[\text{W}^{\text{IV}}\text{O}(\text{W}^{\text{VI}}\text{S}_4)_2]^{2-}$	Red orange	373, 442	40
$[\text{W}^{\text{IV}}\text{S}(\text{W}^{\text{VI}}\text{S}_4)_2]^{2-}$	Golden yellow	271, 392	40

Table 1.5 Bond distances in sulfido and polysulfido complexes

Compound	(S-S) Å	(M-S _D) Å	M---M Å	Reference
[Mo ^{VI} OS ₂ (S ₂ CNEt ₂) ₂]	2.02	-	-	94, 99
[Mo ₂ ^V O ₂ (μ-S) ₂ (S ₂) ₂] ²⁻	2.08	2.825	2.829	100
[Mo ₂ ^V OS(μ-S) ₂ (S ₂) ₂] ²⁻	2.063, 2.069	2.30, 2.33	2.83	39, 49
[Mo ^{IV} S(Mo ^{VI} S ₄) ₂] ²⁻	-	2.086	2.802, 3.082	40, 68
[W ^{VI} S(S ₂)(S ₂ CNEt ₂) ₂]	2.208	-	-	
[W ^{IV} S(μ ^{VI} S ₄) ₂] ²⁻	-	2.07	2.882, 3.047	40, 68
[W ₂ ^V S ₂ (μ-S) ₂ (S ₂) ^{(S₄)₂}] ²⁻	2.84	2.089 2.117	2.84	49
[W ₂ ^V S ₂ (μ-S) ₂ (S ₄) ₂] ²⁻	2.083	2.321	2.834	48, 49
[W ^{III} (W ^{VI} S ₄) ₂] ²⁻	-	2.344	2.871	44

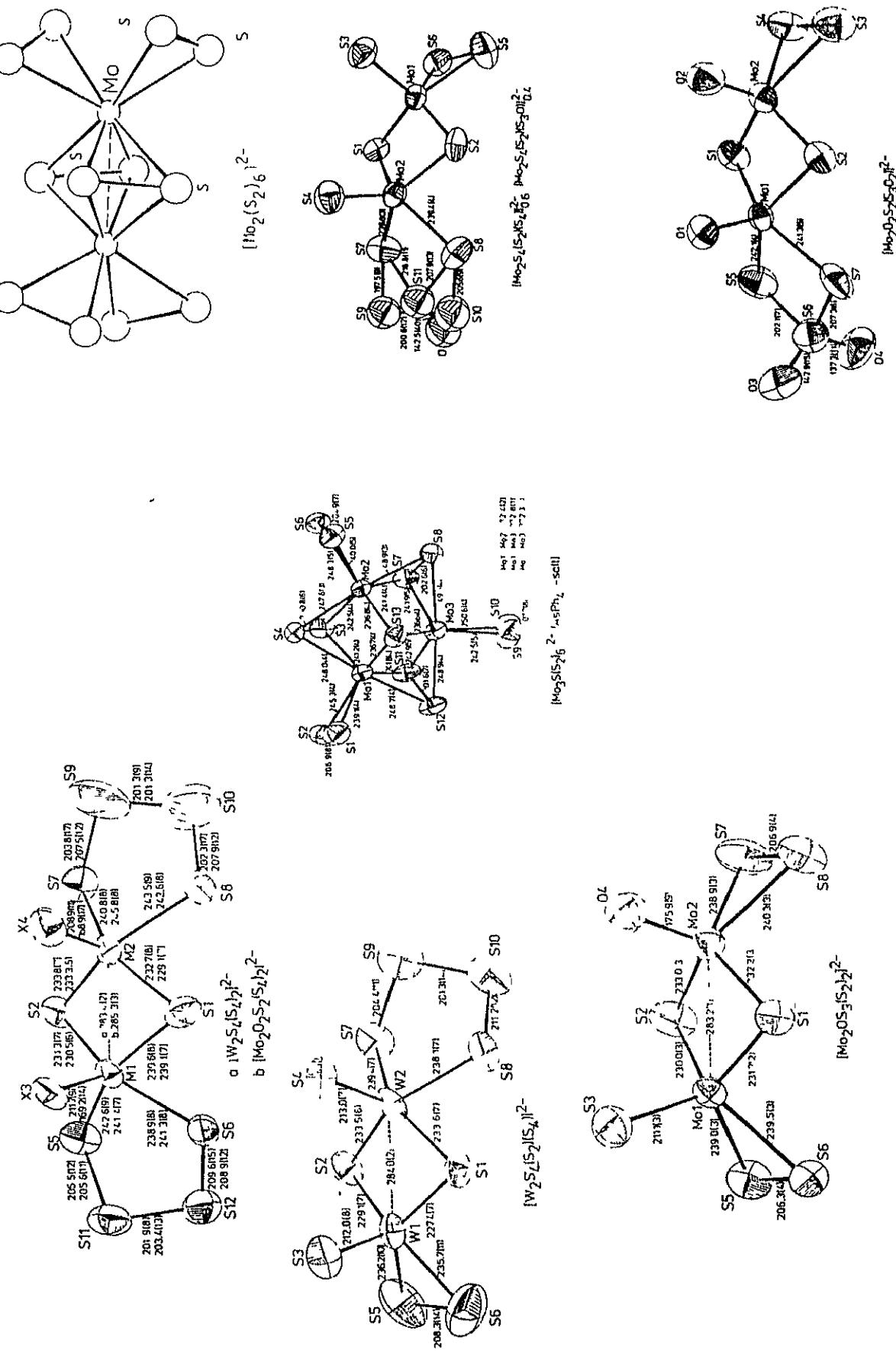
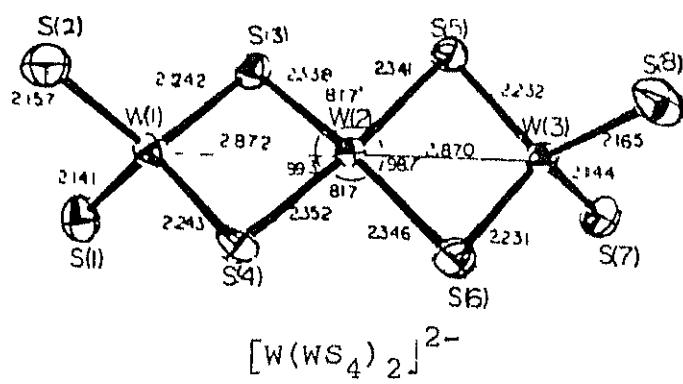
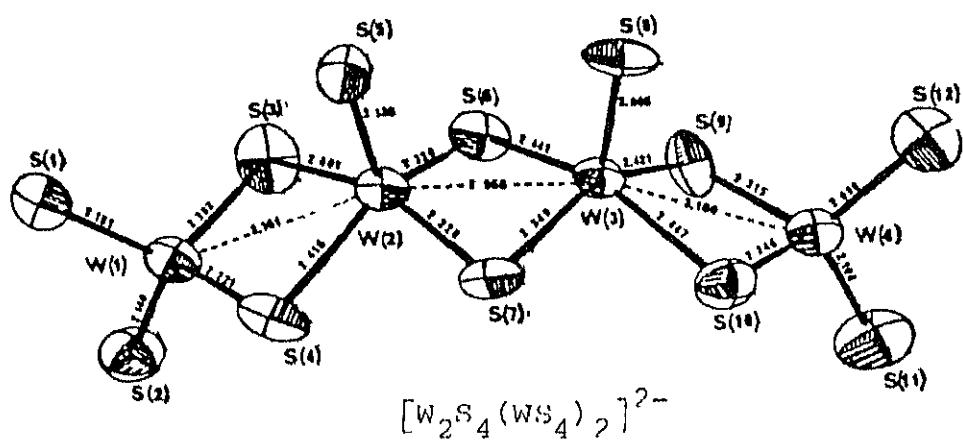
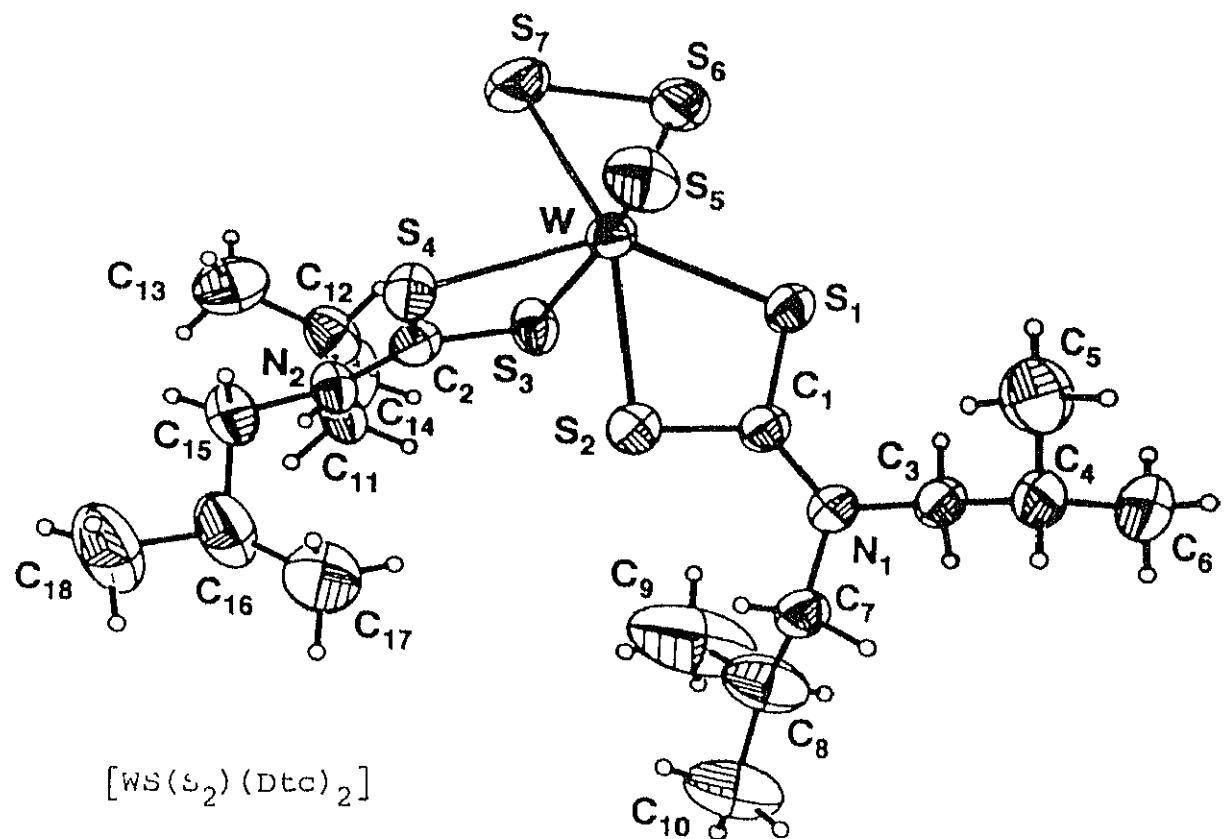


FIG. 1.1 CRYSTAL STRUCTURES



Chapter 2

SCOPE OF THE WORK

The simplest and best studied tetrathiometallates are MoS_4^{2-} and WS_4^{2-} .^{102,103} First example of the intramolecular induced electron transfer in such systems is the synthesis of $[\text{Mo}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ using oxygen as an external oxidant.³⁶ Another interesting reaction is the oxidation of S_x^{2-} ligand by O_2 , leading to the formation of novel ligands like $\text{S}_3\text{O}_2^{2-}$ or S_3O^{2-} .^{37,39} Application of this methodology to tungsten-sulfur systems is a recent phenomenon.^{44,46-48} Intramolecular electron transfer across metal-sulfur bond could be extended to the corresponding tungsten systems by varying the reaction conditions. Keeping the difference between the energy levels of 5d of tungsten and 3p orbital of sulfur in consideration, an appropriate inducing source can be chosen. A broad spectrum of the inducing sources like thermal,^{30,37} photochemical³² or chemical stimuli⁴² may be attempted. The variation of inducing source could be done on two counts:

- i) The redox potential of the external oxidants could be varied.
- ii) Instead of one electron oxidants two electron oxidants could be used.

Of the common oxidants, molecular oxygen seems to be the most important as its role is vital in biological processes.¹⁰⁴ In aprotic medium, acceptance of electrons by molecular oxygen is a stepwise process. The first oxidation product, superoxide radical ion O_2^- functions as a moderate reducing agent whereas in protic medium, the superoxide forms HO_2 , a powerful oxidant.¹⁰⁵ Thus the reaction conditions govern the course of the reaction.

When two electron oxidants are used, the situation may be a little complicated because the reaction might proceed either through an induced electron transfer or in a purely ligand based redox manner. To decide which one is in operation, electrochemical and ESR spectral studies could be helpful. Even if the process involves induced electron transfer, there could be two options for the reaction to proceed, either it can take place in a concerted fashion or in a stepwise manner. Kinetic measurements and C.V. studies can help to resolve such problems to a greater extent.

Reactions of this type are important not only from a mechanistic point of view but also from synthetic considerations. Exploiting this phenomenon, new synthetic strategies can be developed for the preparation of the compounds which are not

accessible through conventional methods.

Tungsten-sulfur chemistry has invited tremendous attention in the recent years mainly because of its importance in:

- i) HDS catalysis, and
- ii) Biology.

HDS (hydrodesulfurization) involves the conversion of S from crude oil fractions or coal-derived liquids in the presence of H_2 into H_2S . Co-Mo and Ni-W units supported on alumina serve as good catalysts.¹⁰⁶⁻¹¹⁰ Activation of the M-bound S_2^{2-} ligand may be of relevance to the HDS reaction, ($M = Mo, W$). This process involves the activation of H_2 and C-S bond cleavage.

The proposed mechanism for HDS reaction is shown in Scheme 2.1.⁸⁰

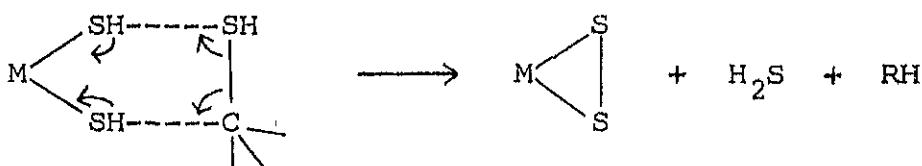
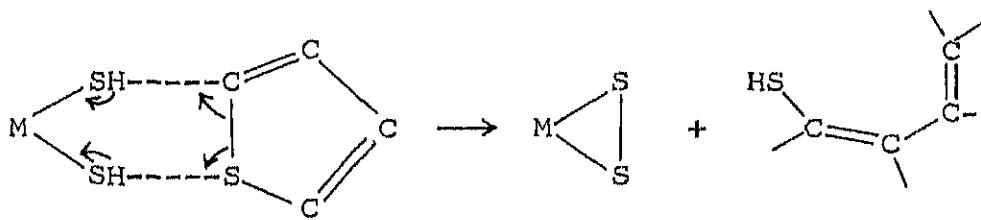
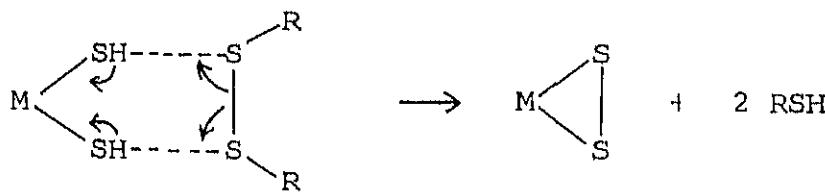
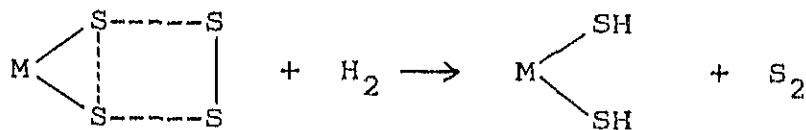
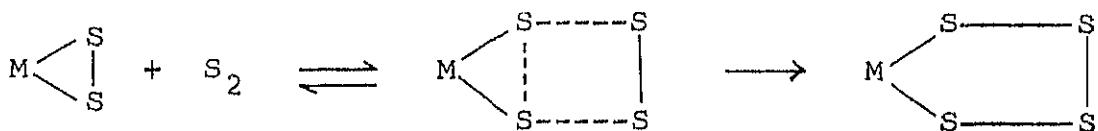
This scheme is in agreement with the work of Dubois and coworkers who demonstrated that appropriately activated S_2^{2-} units in the $(CpMoS_2)_2$ complex are capable of activating H_2 ¹¹¹ and catalyze the reduction of elemental sulfur and hydrogenation of alkynes.¹¹²

Tungsten, the only biologically active member of the 3rd transition series plays a key role in a metalloenzyme, formate-dehydrogenase.¹⁰¹ Modelling of this enzyme, as well as some other molybdoenzymes can be done once the synthetic strategy is developed. Most of the models proposed so far, satisfy neither the structural nor the functional aspects of the enzymes.^{94, 113-116} Hence the search for better models still continues. Some of the molybdoenzymes retain their activity when metal center is

SCHEME 2.1

Possible Reactions of the Activated S_2^{2-} Relevant

to HDS



substituted by tungsten.^{117,118} Thus the first step in the modelling of these enzymes could be the synthesis of a model with tungsten center. The failure in the modelling of the

molybdoenzymes lies mainly in the instability of molybdenum-sulfur systems which can serve as models whereas the corresponding tungsten compounds are generally more stable. Once these are synthesized, various aspects of the system can be studied.

Another aspect of the studies on tungsten-sulfur systems could be to see the trend in the reactivity in the series WS_4^{2-} , WOS_3^{2-} and $WO_2S_2^{2-}$ ions. Substitution of sulfur by oxygen may enhance the sluggishness of the system and a more powerful inducing agent may be needed to invoke the intramolecular electron transfer.

After successfully carrying out the work on tungstensulfur system, the feasibility of transferring the methodology to molybdenum-sulfur systems can be tried. Problems arising at this stage can be handled in two ways:

- i) Nature of the inducing agent can be varied, i.e., a mild inducing agent can be used.
- ii) Size of the coligand can be varied to stabilize the system.

Once the synthetic goal is achieved, the reactivity of the synthesized complexes can be explored. The general guideline to design a reaction would be parallel to molybdenum chemistry where such studies are well documented.^{62-68, 71-77, 119-124}

Chapter 3

SYNTHESIS AND REACTIVITY OF THE COMPLEXES

General Considerations

All the reactions were carried out under dry nitrogen atmosphere unless otherwise specified. Solvents used were of analytical grade and dried before use but not degassed. Dibenzoyl acetylene and dimethyl acetylene dicarboxylate were purchased from Aldrich and used without further purification.

3.1 Methods of Analysis and Work-up Manipulations

Elemental analyses for carbon, hydrogen and nitrogen were done at Microanalytical Laboratory, Indian Institute of Technology, Kanpur. Sulfur was estimated as BaSO_4 and the procedure employed is as follows: The complex containing sulfur (ca. 0.3 g) was treated with an excess of alkaline bromine water. The excess bromine was evaporated off by warming the solution slowly on a water bath. Resulting solution was treated with HCl and the liberated bromine was again evaporated off by boiling the solution slowly. The solution was filtered and the sulfate in the filtrate was estimated by precipitating it as BaSO_4 , in the usual manner.¹²⁵

3.2 Preparation of the Starting Materials

Synthesis of $(\text{NH}_4)_2\text{WS}_4$:

H_2WO_4 (5.0 g) was treated with concentrated NH_4OH (40 ml), the slurry was saturated with H_2S at room temperature and then heated at 60°C with stirring for 20 min. After filtration, the solution was again heated at 60°C and H_2S bubbling continued for 8 hr. The reaction mixture was cooled to 15°C while maintaining the H_2S flow and then the solid product was isolated by filtration, washed with i-PrOH and ether and dried in vacuo,^{103,126} (yield, ~60%). Purity of the compound was checked by electronic spectrum which shows the bands only at 393 and 277 nm (in H_2O).

Synthesis of $(\text{NH}_4)_2\text{WOS}_3$:

H_2WO_4 (5.09 g) was dissolved in a mixture of concentrated NH_4OH (20 ml) and H_2O (5 ml) and the solution was filtered. H_2S was bubbled rapidly into the solution for 15 min. at ambient temperature causing the precipitation of a minimal amount of $(\text{NH}_4)_2\text{WO}_2\text{S}_2$. The reaction mixture was filtered into ice cold i-PrOH (500 ml) and the product separated as a yellow solid which was isolated by filtration, washed with i-PrOH and ether and dried in vacuo,¹²⁶ (yield, ~50%).

The electronic spectrum of the compound gave characteristic bands at 375, 336, 268 and 240 nm (in H_2O).

Synthesis of $(\text{NH}_4)_2\text{WO}_2\text{S}_2$:

H_2WO_4 (5.0 g) was dissolved in a mixture of concentrated NH_4OH (20 ml) and H_2O (5 ml). The solution was filtered and placed in an ice bath. H_2S was passed rapidly over the surface of the solution for 5 min causing the separation of the yellow product which was isolated by filtration, washed with EtOH and ether and dried in vacuo, ¹²⁶ (yield, ~75%).

The electronic spectrum of the compound gave characteristic bands at 326, 272, 246 nm (in H_2O).

Preparation of Methanolic Potassium Polysulfide Solution

To a mixture of potassium hydroxide (4.0 g) and sulfur (20.0 g) in methanol (100 ml), a moderately rapid stream of hydrogen sulfide was passed for two hr. The resulting orange-red solution was filtered to remove the excess sulfur and the polysulfide solution was stored in a stoppered flask.

Synthesis of $(\text{Et}_2\text{NH}_2)_2\text{WS}_4$:

Tungstic acid (5 g) was dissolved in a mixture of H_2O (10 ml) and Et_2NH (15 ml) by refluxing for 1 hr. The solution was filtered and H_2S was passed rapidly for 4 hr at 60°C . When reaction mixture was cooled, yellow crystals separated which were washed with i-PrOH and ether (yield, 7.36 g; 80%).

Anal. Calcd. for $\text{C}_8\text{H}_{24}\text{N}_2\text{S}_4\text{W}$: C, 20.86; H, 5.21; N, 6.08.

Found: C, 20.71; H, 5.42; N, 6.25%.

Synthesis of $(Et_2NH_2)_2WOS_3$:

Tungstic acid (5 g) was refluxed in a mixture of H_2O (10 ml) and Et_2NH (10 ml) for 1.5 hr, filtered, into which H_2S was bubbled rapidly for 50 min, at $60^\circ C$. The solution was cooled and to this iso-propanol (50 ml) and ether (20 ml) were added. The yellow orange oily mass so obtained, was recrystallized from methanol/ether (yield, 6.48 g; 73%).

Anal. Calcd. for $C_8H_{24}N_2OS_3W$: C, 21.62; H, 5.40; N, 6.30.

Found: C, 20.71; H, 5.32; N, 6.28%.

Synthesis of $(Pr_2NH_2)_2WS_4$:

The same procedure was followed except the tungstic acid, water and dipropyl amine mixture was refluxed till all the tungstic acid went into the solution (yield, 63%).

Anal. Calcd. for $C_{12}H_{32}N_2S_4W$: C, 27.90; H, 6.28; N, 5.42.

Found: C, 27.72; H, 6.41; N, 5.32%

Synthesis of $(Pr_2NH_2)_2WOS_3$:

Same procedure as in the case of $(Et_2NH_2)_2WOS_3$, was followed except the tungstic acid, water, amine mixture was refluxed till all the tungstic acid went into the solution (yield, 58%).

Anal. Calcd. for $C_{12}H_{32}N_2OS_3W$: C, 28.80; H, 6.40; N, 5.60.

Found: C, 28.68; H, 6.44; N, 5.13%.

Synthesis of $(\text{C}_6\text{H}_5\text{NH}_2)_2\text{WS}_4$: Same procedure as for the preparation of $(\text{Et}_2\text{NH}_2)_2\text{WS}_4$ was followed except the mixture of tungstic acid, piperidine and water was refluxed till all the tungstic acid dissolved (yield, 78%).

Anal. Calcd. for $\text{C}_{10}\text{H}_{24}\text{N}_2\text{S}_4\text{W}$: C, 24.79; H, 4.95; N, 5.78.

Found: C, 24.58; H, 4.78; N, 5.72%.

Synthesis of $(\text{C}_6\text{H}_5\text{NH}_2)_2\text{WOS}_3$: Similar methodology was adopted as in the case of $(\text{Et}_2\text{NH}_2)_2\text{WOS}_3$, except the mixture of tungstic acid, piperidine and water was refluxed till all the tungstic acid went into solution (yield, 61%).

Anal. Calcd. for $\text{C}_{10}\text{H}_{24}\text{N}_2\text{OS}_3\text{W}$: C, 25.64; H, 5.12; N, 5.98.

Found : C, 25.62; H, 5.10; N, 5.90%.

3.3.1 Induced Electron Transfer Reactions

Synthesis of $(\text{Et}_4\text{N})_2[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]$ - Method 'A'

$(\text{NH}_4)_2\text{WOS}_3$ (664 mg; 2 mmol) and Et_4NBr (630 mg; 3 mmol) were dissolved in H_2O (20 ml) and iodine (253.8 mg; 2 mmol) was added to it. The mixture was warmed on the water bath for 20 min, then KOH (100 mg; 2.56 mmol) was added to it. After 5 min the solution was filtered and the precipitate was washed with H_2O , EtOH and ether and was recrystallized from $\text{CH}_3\text{CN}/i\text{-PrOH}$ (yield, 180 mg; 21.12%).

Anal. Calcd. for $\text{C}_{16}\text{H}_{40}\text{N}_2\text{O}_2\text{S}_6\text{W}_2$: C, 22.53; H, 4.69; N, 3.28; S, 22.53.

Found: C, 22.49; H, 4.52; N, 3.08; S, 22.62%.

Synthesis of $(Et_4N)_2[W_2O_2(\mu-S)_2(S_2)_2]$ - Method 'B'

$(NH_4)_2WOS_3$ (664 mg; 2 mmol) was dissolved in H_2O (30 ml) and solid $(NH_4)_2S_2O_8$ (228.20 mg; 1 mmol) was added shaking the solution vigorously. Solution was stirred for 4 hr and Et_4NBr (630 mg; 3 mmol) was added to it. After 10 min a 25% ammonia solution (5 ml) was added to it. This was filtered and the precipitate was washed and recrystallized as mentioned above (yield, 205 mg; $\sim 24\%$). Analysis was found to be satisfactory.

Synthesis of $(Et_4N)_2[W_2O_2(\mu-S)_2(S_2)_2]$ - Method 'C'

$(NH_4)_2WOS_3$ (664 mg, 2 mmol) and Et_4NBr (630 mg; 3 mmol) were dissolved in DMF (20 ml) and warmed at $110^\circ C$ for 5 min. $C_6H_5-S-S-C_6H_5$ (218.34 mg; 1 mmol) or $(C_2H_5)_2N-CSSSSC-N(C_2H_5)_2$ (296.54 mg; 1 mmol) or t-butyl hydroperoxide (0.1 ml; ~ 1 mmol) or $C_6H_5-O-O-C_6H_5$ (186.21 mg; 1 mmol) was added to it. The resulting red solution was left at $110^\circ C$ for 1/2 hr. Addition of i-PrOH (15 ml) and ether (30 ml) yielded red crystalline product which was washed with H_2O , EtOH and ether and recrystallized from CH_3CN/i -PrOH (yield, $\sim 70\%$). Analysis was found to be satisfactory.

Synthesis of $(Me_4N)_2[W_2O_2(\mu-S)_2(S_2)_2]$

$(NH_4)_2WOS_3$ (668 mg; 2 mmol) dissolved in DMF (15 ml), Me_4NCl (219 mg; 2 mmol) dissolved in H_2O (5 ml) were mixed. This was warmed at $110^\circ C$ for 5 min and $C_6H_5-S-S-C_6H_5$ (216.34 mg; 1 mmol) was added to this solution. After 1/2 hr colour of the

solution darkened and then became orange. It was then cooled and i-PrOH (20 ml) and ether (20 ml) was added and left for 1 hr. The yellow product which separated out was washed with H_2O , ethanol, and ether and recrystallized from CH_3CN/i -PrOH (yield, 426 mg; 57.56%).

Anal. Calcd. for $C_8H_{24}N_2O_2S_6W_2$: C, 12.97; H, 3.24; N, 3.78; S, 25.94.

Found: C, 12.85; H, 3.25; N, 3.16; S, 25.80%.

Synthesis of $(Et_4N)_2[WS(WS_4)_2]$ - Method 'A'

To a solution of $(NH_4)_2WS_4$ (1.044 g; 3 mmol) and Et_4NBr (630 mg; 3 mmol) in H_2O (30 ml), $(NH_4)_2S_2O_8$ (228.20 mg; 1 mmol) was added, stirring the solution vigorously. Some red precipitate was thrown out immediately. Further stirring for 1 hr gave some more product which was filtered, washed with EtOH and ether and was recrystallized from CH_3CN/i -PrOH (yield, 310 mg; ~30%).

Anal. Calcd. for $C_{16}H_{40}N_2S_9W_3$: C, 17.45; H, 3.63; N, 2.54; S, 26.18.

Found: C, 17.52; H, 3.42; N, 2.50; S, 26.10%.

Synthesis of $(Et_4N)_2[WS(WS_4)_2]$ - Method 'B'

$(NH_4)_2WS_4$ (1.644 g; 3 mmol) and Et_4NBr (630 mg; 3 mmol) were dissolved in DMF (15 ml) and the solution was warmed at $110^\circ C$ for 5 min. $(C_6H_5S)_2$ (218.34 mg; 1 mmol) was added to the above solution with shaking. It was then cooled to room temperature. Addition of i-PrOH (20 ml) and ether (50 ml) yielded a

dark red crystalline product which was washed and recrystallized as mentioned above (yield, 605 mg; ~58%).

Synthesis of $(\text{Ph}_4\text{As})_2[\text{WS}(\text{WS}_4)_2]$

$(\text{NH}_4)_2\text{WS}_4$ (1.044 g; 3 mmol), $\text{Ph}_4\text{AsCl} \cdot \text{HCl}$ (1.146 g; 2 mmol) and NaOH (80 mg; 2 mmol) were dissolved in DMF (15 ml) and warmed at 110°C for 10 min followed by the addition of $\text{C}_6\text{H}_5\text{-S-S-C}_6\text{H}_5$ (218.34 mg; 1 mmol). On shaking colour of the solution became dark red. To the cold solution i-PrOH (20 ml) and ether (100 ml) was added. Red oily product thus obtained was repeatedly washed with EtOH and was recrystallized from $\text{CH}_3\text{CN}/\text{i-PrOH}$ (yield, 652 mg; 39.52%).

Anal. Calcd. for $\text{C}_{48}\text{H}_{40}\text{S}_9\text{As}_2\text{W}_3$: C, 40.50; H, 2.81.

Found: C, 40.62; H, 2.48%.

Synthesis of $(\text{Et}_4\text{N})_2[\text{WO}(\text{WS}_4)_2]$

$(\text{NH}_4)_2\text{WS}_4$ (1.044 g; 3 mmol) dissolved in DMF (15 ml) and Et_4NBr (630 mg; 3 mmol) dissolved in H_2O (5 ml) were mixed and heated at 110°C for 15 min. To the above solution $\text{C}_6\text{H}_5\text{-S-S-C}_6\text{H}_5$ (218 mg, 1 mmol) was added and heated for a further 10 min. The resulting solution was cooled at room temperature and i-PrOH (10 ml) and ether (50 ml) were added to it. The orange product that separated out was washed with water, EtOH and finally with ether (yield, 410 mg, ~40%).

Analysis and spectral results are similar to that of the same compound reported earlier.¹²⁸

Synthesis of $(\text{PhCH}_2)(\text{C}_2\text{H}_5)_3\text{N}_2[\text{WO}(\text{WS}_4)_2]$

$(\text{NH}_4)_2\text{WS}_4$ (1.044 g; 3 mmol) dissolved in DMF (15 ml) and $[(\text{PhCH}_2)(\text{C}_2\text{H}_5)_3\text{N}]\text{Br}$ (484 mg; 2 mmol) dissolved in H_2O (5 ml) were mixed and heated at 110°C for 10 min. followed by addition of $\text{C}_6\text{H}_5\text{-S-S-C}_6\text{H}_5$ (218 mg, 1 mmol) and heating for a further 10 min. To the cold solution i-PrOH (10 ml) and ether (50 ml) were added which gave oily mass. It was washed with EtOH and recrystallized from $\text{CH}_3\text{CN}/\text{i-PrOH}$ (yield, 392 mg; 32.45%).

Anal. Calcd for $\text{C}_{26}\text{H}_{44}\text{N}_2\text{OS}_8\text{W}_3$: C, 25.82; H, 3.64; N, 2.31; S, 21.19.

Found: C, 25.77; H, 3.42; N, 2.45; S, 21.22%.

Synthesis of $((2\text{-Cl.C}_2\text{H}_4)(\text{CH}_3)_2\text{.NH}_2[\text{WO}(\text{WS}_4)_2]$

A mixture $(\text{NH}_4)_2\text{WS}_4$ (1.044 g; 3 mmol) in DMF (15 ml) and $[(2\text{-Cl.C}_2\text{H}_4)(\text{CH}_3)_2\text{.NH}]\text{Cl}$ in H_2O (2 ml) was heated at 110°C for five min. and $\text{C}_6\text{H}_5\text{-S-S-C}_6\text{H}_5$ (218.34 mg; 1 mmol) was added to it. After 1/2 hr when the colour of the solution became red, it was cooled to room temperature and i-PrOH (20 ml) and ether (40 ml) was added. An orange product separated out, which on washing with H_2O , EtOH and ether, and thereafter recrystallization from $\text{CH}_3\text{CN}/\text{i-PrOH}$ yielded 565 mg (61.08%) of the desired compound.

Anal. Calcd. for $\text{C}_8\text{H}_{22}\text{N}_2\text{OS}_8\text{W}_3$: C, 10.37; H, 2.37; N, 3.02; S, 27.66.

Found: C, 10.58; H, 2.51; N, 2.80; S, 27.52%.

3.3.2 Reactivity of the Synthesized Complexes

Reactivity of $(Et_4N)_2[W_2O_2S_6]$ with DBA or Synthesis of $(Et_4N)_2^-$ $[W_2O_2(\mu-S)_2(S_2C_2(COPh)_2)_2]$

Dibenzoyl acetylene (DBA) (234 mg; 1 mmol) was dissolved in CH_3CN (5 ml) and added to a solution of $[Et_4N]_2W_2O_2S_6$ (426 mg; 0.5 mmol) in CH_3CN (10 ml) and stirred for 5 min. When colour of the solution changed from orange to green, it was cooled to R.T. and EtOH was added dropwise till the solution became turbid. It was filtered and the filtrate was kept at R.T. for 2 days. Dark red needle shaped crystals separated out which were washed with EtOH and ether and dried under vacuum (yield, 130 mg, 19.7%).

Anal. Calcd. for $C_{48}H_{60}N_2O_6S_6W_2$: C, 43.63; H, 4.54; N, 2.12.

Found: C, 43.59; H, 4.52; N, 2.04%.

Reactivity of $(Et_4N)_2[W_2O_2S_6]$ with DMA or Synthesis of $(Et_4N)_2^-$ $[W_2O_2(\mu-S)_2(S_2C_2(COOMe)_2)_2]$

To a solution of $(Et_4N)_2[W_2O_2(\mu-S)_2(S_2)_2]$ (426 mg, 0.5 mmol) in CH_3CN (10 ml) dimethyl acetylene dicarboxylate (DMA), (0.13 ml, 1 mmol) was added and the solution was shaken well. The colour of the solution changed immediately from yellow to brown to green. After 5 hr absolute ethanol was added dropwise till it became turbid. It was left at R.T. for 2 days and the precipitate thus formed was washed with EtOH and ether and vacuum dried (yield, 230 mg, 42.91%).

Anal. Calcd. for $C_{28}H_{52}N_2O_6S_6W_2$: C, 31.34; H, 4.85; N, 2.61.
 Found : C, 31.62; H, 4.76; N, 2.52%.

Synthesis of $(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$

$(Et_4N)_2WS_4$ (190.6 mg; 1/3 mmol), sulfur (21.33 mg, 3/2 mmol) and dibenzoyl acetylene (234 mg; 1 mmol) were taken in DMF (10 ml) and the solution was stirred for 12 hr. The colour of the solution changed from red to brown to greenish brown. Addition of iso-propanol till the solution became turbid, and leaving it at room temperature for 24 hr gave greenish brown crystals, which were washed with EtOH, CS_2 and ether, and dried under vacuum, yield, 165 mg (37%).

Anal. Calcd. for $C_{64}H_{70}N_2O_6S_6W$: C, 57.39; H, 5.23; N, 2.09.
 Found: C, 56.65; H, 5.13; N, 1.89%.

Synthesis of $K_4[W_2O_2(\mu-S)_2(CN)_6] \cdot 3H_2O$

A suspension of $(Et_4N)_2[W_2O_2S_6]$ (852 mg; 1 mmol), potassium cyanide (2 g; 30.7 mmol) in H_2O (10 ml) was stirred for 10 min. The colour of the solution changes from green to brown and finally to bright yellow. Addition of i-PrOH (20 ml) gave some oily mass

which was recrystallized from H_2O and EtOH. Yellow crystals thus formed, were washed with ethanol and ether, and dried in vacuum; yield 600 mg (73.89%).

Anal. Calcd. for $C_6H_6N_6O_5S_2K_4W_2$: C, 8.67; H, 0.72; N, 10.12.

Found: C, 9.20; H, 0.81; N, 10.05;

3.4.1 Induced Electron Transfer Reactions Concealed Under Ligand Based Redox Processes

Synthesis of $[WO(S_2)(S_2CNET_2)_2]$ - Method 'A'

A solution of $(Et_2NH_2)_2WOS_3$ (444 mg; 1 mmol) in DMF (10 ml) was stirred with CS_2 (2 ml) for 36 hr in the presence of air. This solution was filtered and i-PrOH (50 ml) was added to it. This was kept at room temperature for 24 hr. Brown crystalline product was thrown out, which was purified by flash chromatography on silica gel using $CHCl_3$ and petroleum ether (60:40) as eluant (yield, 390 mg; ~70%).

Anal. Calcd. for $C_{10}H_{20}N_2OS_6W$: C, 21.43; H, 3.57; N, 5.00.

Found: C, 21.60; H, 3.60; N, 4.72%.

Synthesis of $[WO(S_2)(S_2CNET_2)_2]$ - Method 'B'

$(NH_4)_2WO_2S_2$ (316 mg; 1 mmol) was dissolved in DMF (15 ml) by warming it on a hot plate. The solution was cooled and

tetraethylthiuram disulfide (296.54 mg; 1 mmol) was added to it. The solution was filtered, and i -PrOH (10 ml), ether (200 ml) were added to it. Keeping the solution in the refrigerator for 4 days, yielded brown crystalline product. The crystals were washed with i -PrOH, ether and dried under vacuum (yield, 55 mg (9.82%). Analysis was found to be the same as in method 'A'.

Synthesis of $[\text{WO}(\text{S}_2)(\text{S}_2\text{CNPr}_2)_2]$

A solution of $(\text{Pr}_2\text{NH}_2)_2\text{WOS}_3$ (500 mg; 1 mmol) in DMF (10 ml) was stirred with CS_2 (2.5 ml) for 40 hr in the presence of air at room temperature. The solution was poured into water (150 ml). The oily material was extracted in CHCl_3 and was purified by flash chromatography on silica gel using CHCl_3 :petroleum ether mixture (50:50) (yield, 230 mg; 37.95%) as eluant.

Anal. Calcd. for $\text{C}_{14}\text{H}_{28}\text{N}_2\text{S}_6\text{OW}$: C, 27.27; H, 4.54; N, 4.54.

Found: C, 27.10; H, 4.60; N, 4.60%.

Synthesis of $[\text{WO}(\text{S}_2)(\text{S}_2\text{CN}\text{C}_6\text{H}_4)_2]$

$(\text{PipH})_2\text{WOS}_3$ (468 mg; 1 mmol) was dissolved in DMF (10 ml) and stirred with CS_2 (3 ml) for 24 hr at room temperature. Addition of i -PrOH (10 ml) and ether (100 ml) resulted in the precipitation of a brown product which was washed with H_2O , EtOH, ether and was purified by flash chromatography using CHCl_3 :petroleum ether as eluant (yield, 258 mg; 44.17%).

Anal. Calcd. for $C_{12}H_{20}N_2OS_6W$: C, 24.65; H, 3.42; N, 4.79; S, 32.87.

Found: C, 24.24; H, 3.35; N, 4.60; S, 32.96%.

Synthesis of $[WS(S_2)(S_2CNET_2)_2]$

$(Et_2NH_2)_2WS_4$ (460 mg; 1 mmol) was dissolved in DMF (10 ml) and CS_2 (2 ml) was added to it. The resultant red solution was stirred in the presence of air at room temperature for 36 hr. The solution was filtered and i-PrOH (50 ml) and ether (10 ml) were added to it. Keeping the resulting solution at $25^\circ C$ for 24 hr resulted in the separation of green crystalline product. This was washed with H_2O , EtOH, ether and dried under vacuum. The compound was purified by flash chromatography on silica gel using $CHCl_3$:petroleum ether (60:40) as eluant (yield, 282 mg; 48.92%).

Anal. Calcd. for $C_{10}H_{20}N_2S_7W$: C, 20.83; H, 3.47; N, 4.86.

Found: C, 20.86; H, 3.72; N, 4.52%.

Synthesis of $[WS(S_2)(S_2CNPr_2)_2]$

$(Pr_2NH_2)_2WS_4$ (348 mg; 1 mmol) taken in DMF (5 ml) was stirred with CS_2 (2 ml) for 48 hr. When the solution became dark green, it was poured into water (100 ml). The crude product precipitated out which was washed with H_2O , i-PrOH:ether mixture (80:20) and finally with ether. Purification by flash chromatography on silica gel using $CHCl_3$:petroleum ether (40:60) as eluant gave the

green compound (yield, 115 mg; 18.2%).

Anal. Calcd. for $C_{14}H_{28}N_2S_7W$: C, 26.58; H, 4.43; N, 4.43.

Found: C, 25.96; H, 4.46; N, 4.31%.

Synthesis of $[WS(S_2)(S_2CN\text{C}_6H_{11})_2]$

$(\text{PipH})_2WS_4$ taken in DMF (10 ml) was mixed with CS_2 (2 ml) and stirred vigorously for 38 hr. The solution was filtered and to the filtrate i-PrOH (10 ml) and ether (150 ml) were added to get the green crude product. It was washed with H_2O , EtOH and ether, and purified by flash chromatography using $CHCl_3$: petroleum ether (50:50) as eluant (yield, 210 mg; 35%).

Anal. Calcd. for $C_{12}H_{20}N_2S_7W$: C, 24.00; H, 3.33; N, 4.66.

Found: C, 24.21; H, 3.20; N, 4.56%.

Synthesis of $(Et_2NH_2)[WO(S_2)_2(S_2CNET_2)]$ - Method 'A'

$(Et_2NH_2)_2WS_4$ (460 mg; 1 mmol) was dissolved in DMF (5 ml) and CS_2 (1 ml) was added to it. The resulting red solution was stirred for 16 hr in the presence of air. Addition of i-PrOH (50 ml) and ether (180 ml) and on keeping it at room temperature overnight resulted in the separation of reddish brown crystalline product which was washed with H_2O , i-PrOH and finally with ether and recrystallized from acetone/petroleum ether (yield, 260 mg; 47.3%).

Anal. Calcd. for $C_9H_{22}N_2OS_6W$: C, 19.63; H, 4.00; N, 5.09.

Found: C, 19.25; H, 3.75; N, 5.05%.

Synthesis of $(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$ - Method 'B'

$(NH_4)_2WS_4$ (348 mg; 1 mmol) was dissolved in DMF (10 ml) and heated upto $130^\circ C$ and to this tetraethylthiuram disulfide (296.54 mg; 1 mmol) was added. The solution was cooled to room temperature. To this iso-propanol (20 ml) and ether (150 ml) were added. Further cooling of the resultant solution to $5^\circ C$ and keeping it at the same temperature for 24 hr gave reddish brown crystalline product along-with microcrystalline red product. The reddish brown product was extracted in acetone (20 ml) and was precipitated by adding petroleum ether (20 ml) (yield, 60 mg; 10.9%). The analytical data was identical with that of the compound obtained from method 'A'.

Synthesis of $(Pr_2NH_2)[WO(S_2)_2(S_2CNPr_2)]$

$(Pr_2NH_2)_2WS_4$ (516 mg; 1 mmol), was dissolved in DMF (5 ml) and CS_2 (1 ml) was added to it. Resultant red solution was stirred for 24 hr. Addition of iso-propanol (10 ml) and ether (200 ml) and keeping the solution mixture for 3 days yielded dark brown needle shaped crystals which were washed with iso-propanol:ether mixture (50:50) and then finally with ether (yield, 90 mg; 14.85%).

Anal. Calcd. for $C_{13}H_{30}N_2S_6OW$: C, 25.74; H, 4.94; N, 4.62.

Found: C, 25.62; H, 5.00; N, 4.51%.

3.4.2 Reactivity of the Synthesized Complexes

Reactivity of $[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$ with KCN or Synthesis of $[\text{WO}(\text{S}_2\text{CNET}_2)_2]$

$[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$ (280 mg; 0.5 mmol) was dissolved in dichloromethane (10 ml) and KCN (65 mg; 1 mmol) was dissolved in H_2O (5 ml) and EtOH (5 ml). Both the solutions were mixed and stirred vigorously for 6 hr. Partial evaporation of the solution gave a white crystalline product. The crystals were washed with H_2O and dried under vacuum (yield, 90 mg; 36.29%).

Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{OS}_4\text{W}$: C, 24.19; H, 4.03; N, 5.64.

Found: C, 24.10; H, 3.72; N, 5.56%.

Reactivity of $[\text{WO}(\text{S}_2)(\text{S}_2\text{CN} \text{C}_6\text{H}_5)_2]$ with KCN or Synthesis of $[\text{WO}(\text{S}_2\text{CN} \text{C}_6\text{H}_5)_2]$

$[\text{WO}(\text{S}_2)(\text{S}_2\text{CN} \text{C}_6\text{H}_5)_2]$ (292 mg; 0.5 mmol) dissolved in dichloromethane (10 ml) and KCN (65 mg; 1 mmol) dissolved in H_2O (5 ml) and EtOH (5 ml) were mixed and stirred vigorously for 6 hr. Partial evaporation of the solution gave white crystalline product. The product was washed well with H_2O and dried under vacuum (yield, 110 mg; ~42%).

Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{OS}_4\text{W}$: C, 27.69; H, 3.84; N, 5.38.

Found: C, 27.80; H, 3.73; N, 5.22%.

Reaction of $[\text{WO}(\text{S}_2\text{CNET}_2)_2]$ with Elemental Sulfur

$[\text{WO}(\text{S}_2\text{CNET}_2)_2]$ (496 mg; 1 mmol) was dissolved in acetone and sulfur (64 mg; 2 mmol) was added to it. Solution mixture was refluxed for 10 hr and solvents were evaporated. The solid so obtained was recrystallized from CHCl_3 /pet. ether. The compound gave satisfactory analytical results for $[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$ (vide supra).

Reaction of $[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$ with PhSH

$[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$ (560 mg; 1 mmol) was dissolved in CH_2Cl_2 and PhSH (0.2 ml ; 2 mmol) was added. The solution was stirred for 20 hr. Addition of Et OH (20 ml) resulted in the separation of yellow precipitate. This was washed with Et OH and ether and then recrystallized from CH_2Cl_2 /pet. ether. On the basis of spectral and elemental analysis, the product was identified as $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ (vide infra).

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3.5.1 Thermally Induced Electron Transfer Reactions

Synthesis of $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ - Method 'A'

To a solution of $(\text{Et}_2\text{NH}_2)_2\text{WOS}_3$ (888 mg; 2 mmol) in DMF (10 ml), CS_2 (2 ml) was added and the mixture was refluxed for 4 hr. Addition of 1-PrOH (10 ml) and ether (100 ml) to the cold solution, precipitated a small amount of green brown product which was filtered off and the filtrate was kept overnight at room temperature to yield the desired compound as yellow needles. The

compound was washed with H_2O , EtOH and ether and purified chromatographically using CH_2Cl_2 /pet. ether (80:20) as eluant (yield, 290 mg; 38%).

Anal. Calcd. for $C_{10}H_{20}N_2O_2S_6W_2$: C, 15.78; H, 2.63; N, 3.68.

Found : C, 15.90; H, 2.81; N, 3.48%.

Synthesis of $[W_2O_2(\mu-S)_2(S_2CNET_2)_2]$ - Method 'B'

To a hot solution ($130^\circ C$) of $(NH_4)_2WO_2S_2$ (632 mg; 2 mmol) in DMF (10 ml) tetraethylthiuram disulfide (296 mg; 1 mmol) dissolved in DMF (5 ml) was added and the solution was cooled to $25^\circ C$. Addition of i -PrOH (20 ml) and ether (160 ml) and keeping it at $5^\circ C$ for 48 hr, yielded yellow product which was purified as described above (yield, 340 mg; $\sim 45\%$).

Synthesis of $[W_2O_2(\mu-S)_2(S_2CN\text{C}_5H_9)_2]$

To a hot solution ($130^\circ C$) of $(NH_4)_2WO_2S_2$ (632 mg; 2 mmol) in DMF (15 ml), dicyclopentamethylenethiuram disulfide (320.6 mg; 1 mmol) dissolved in DMF (5 ml) was added. The solution was cooled immediately to room temperature and i -PrOH (15 ml) and ether (150 ml) were added to it. Keeping the solution at $5^\circ C$ for 24 hr yielded a yellow powder which was washed with H_2O , EtOH and ether and purified chromatographically using CH_2Cl_2 /pet. ether (70:30) as eluant (yield, 180 mg; $\sim 23\%$).

Anal. Calcd. for $C_{12}H_{20}N_2O_2S_6W_2$: C, 18.36; H, 2.55; N, 3.57.

Found : C, 18.50; H, 2.44; N, 3.21%.

Synthesis of $[\text{W}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ - Method 'A'

A solution of $(\text{Et}_2\text{NH}_2)\text{WS}_4$ (920 mg; 2 mmol) DMF (10 ml) and CS_2 (2 ml) was refluxed for 4 hr under dry nitrogen atmosphere and in the absence of light. To the cold solution (25°C), $i\text{-PrOH}$ (10 ml) and ether (100 ml) were added. A small amount of dark brown product precipitated out which was filtered off. The filtrate was left at room temperature for 24 hr to yield the desired compound as dark red needle shaped crystals. The compound was washed with H_2O , EtOH and ether and purified chromatographically using $\text{CH}_2\text{Cl}_2/\text{pet. ether}$ (75:25) as eluant (yield 220 mg; 28%).

Anal. Calcd. for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_8\text{W}_2$: C, 15.15; H, 2.52; N, 3.53.

Found: C, 15.45; H, 2.40; N, 3.68%.

Synthesis of $[\text{W}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ - Method 'B'

Tetraethylthiuram disulfide (296 mg; 1 mmol) dissolved in DMF (5 ml) was added to a solution of $(\text{NH}_4)_2\text{WS}_4$ (696 mg; 2 mmol) in DMF (10 ml) at 130°C under dry nitrogen atmosphere. To the cold solution (25°C) $i\text{-PrOH}$ (10 ml) and ether (250 ml) were added and kept at 5°C for 25 hr. The crude product thus obtained was washed and purified as described above (yield, 96 mg; 12%). Analysis was found to be satisfactory.

Synthesis of $[\text{W}_2\text{OS}(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$

The same procedure as for the preparation of $[\text{W}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ (method A) was followed except that the reaction was

carried out in the presence of air. The desired compound was obtained as major product (234 mg; ~30%) after chromatographic purification. However, if method B synthesis of $[\text{W}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ is followed in the presence of air, the desired product is obtained in low yield (90 mg; ~12%).

Anal. Calcd. for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{OS}_3\text{W}_2$: C, 15.46; H, 2.57; N, 3.60.

Found: C, 15.78; H, 2.50; N, 3.72%.

Synthesis of $[\text{W}_2\text{OS}(\mu\text{-S})_2(\text{S}_2\text{CNC}_5\text{H}_9)_2]$

$(\text{NH}_4)_2\text{WS}_4$ (696 mg; 2 mmol) was dissolved in DMF (10 ml) and heated in the presence of air at 130°C for 2 min. Dicyclopentamethylenethiuram disulfide (320.6 mg; 1 mmol) was dissolved in DMF (5 ml). Both the solutions were mixed and cooled to room temperature immediately. Addition of *i*-PrOH (20 ml) and ether (150 ml) and keeping at 5°C for 24 hr yielded an orange product which was purified chromatographically using $\text{CH}_2\text{Cl}_2/\text{pet. ether}$ (75:25) as eluant (yield, 180 mg; ~23%).

Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{OS}_7\text{W}$: C, 18.00; H, 2.50; N, 3.50.

Found: C, 19.63; H, 2.46; N, 3.46%.

Disproportionation Reaction of $[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$ or Synthesis of $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ by Thermal Induction

$[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$ (560 mg; 1 mmol) was dissolved in DMF (10 ml) and warmed on a water bath for 1 hr. The colour of the solution faded from brown to yellow. The yellow compound was

isolated by precipitating it by adding 1-ProH (20 ml) and ether (200 ml) to the solution and recrystallizing from CH_2Cl_2 /pet.ether (yield, 265 mg; ~70%).

Disproportionation Reaction of $(\text{Et}_2\text{NH}_2)[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)]$ or
Synthesis of $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ by Thermal Induction

$(\text{Et}_2\text{NH}_2)[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)]$ (550 mg; 1 mmol) was dissolved in DMSO (10 ml) and warmed on a water bath for 30 min. The colour of the solution changed from red brown to yellow. The reaction mixture was poured into water (100 ml). The solid obtained was filtered, washed with EtOH, CS_2 and ether, dried and recrystallized from CH_2Cl_2 /pet. ether. The compound thus obtained gave satisfactory elemental analysis.

3.5.2 Reactivity of the Synthesized Complex

Reaction of $[\text{W}_2\text{OS}(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ with KCN

A suspension of $[\text{W}_2\text{OS}(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ (776 mg; 1 mmol), KCN (65 mg; 1 mmol) and Et_4NBr (210 mg; 1 mmol) in CHCl_3 (50 ml), EtOH (15 ml) and H_2O (5 ml) was refluxed for 96 hr. The solvents were evaporated and the residue was washed with H_2O , MeOH and ether. The bright yellow powder was dried and recrystallized from CH_2Cl_2 /pet. ether. The compound gave elemental analysis and spectral results identical to that of $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$. The aqueous extract gave a positive test for the presence of SCN^- .

Chapter 4

RESULTS AND DISCUSSION

Physical Measurements

Infrared spectra

Infrared spectra of the samples were recorded on a Perkin-Elmer Model-580 infrared grating spectrophotometer. Samples were prepared as CsI pellets and referenced to polystyrene bands.

Electronic spectra

Electronic spectra were recorded on Cary 17D and Shimadzu UV-190 double beam spectrophotometer using matched quartz cells.

NMR spectra

^1H NMR spectra were taken on Varian EM-390, 90 MHz spectrometer and ^{13}C NMR spectra were recorded on Varian CFT-20 400 MHz spectrometer.

ESR Spectra

Electron spin resonance spectra were obtained on a Varian E-109 EPR system (X-band) using DPPH as calibrant.

C.V. Studies

Voltammetric measurements were done on PAR model 370-4 electrochemistry system: 174-A, polarographic analyzer; 175, Universal programmer; REOO74, XY recorder. All experiments were done under dinitrogen atmosphere in a three-electrode configuration using platinum and glassy-carbon working electrodes in +ve and -ve potential region. All results were collected at 298 K and referenced to a saturated calomel electrode (SCE). The reported results are uncorrected for junction contribution.

X-Ray Studies

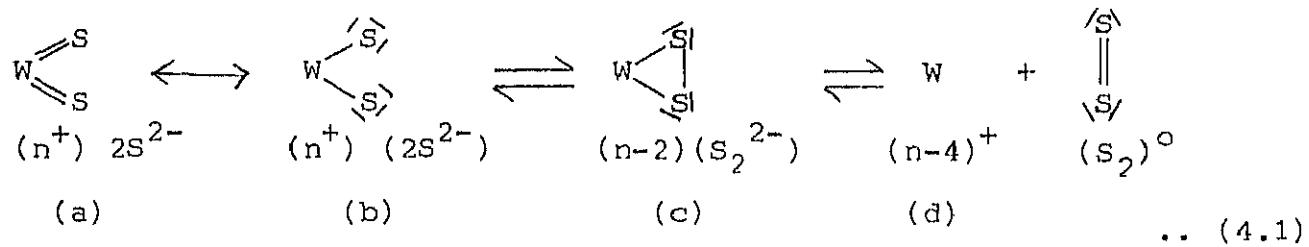
X-ray diffractograms were taken on Siefert ISO-DEBYFLEX X-200 diffractometer using $\text{Cu-K}\alpha$ as radiation source. Samples were fixed on an aluminium planchet. XPS measurements were carried out on ESCALAB 510 photoelectron spectrometer using the $\text{Al-K}\alpha$ line (1486.6 e.v.) radiation.* X-ray structure of $(\text{Et}_2\text{NH}_2)^-[\text{WO}(\text{S}_2)^2(\text{S}_2\text{CNET}_2)]$ was solved by conventional heavy-atom methods.* Diffraction data were collected using Syntex P2₁-diffractometer (ω -scan, at 21°C).

4.1 Redox Based Synthetic Aspects of the Present Work

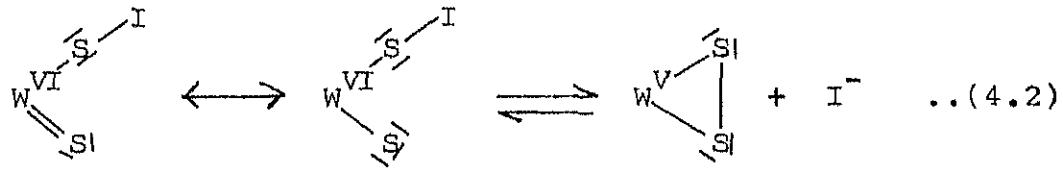
The electronic spectrum of WS_4^{2-} shows the lowest energy charge transfer band at 393 nm.¹²⁶ The corresponding absorption

*Courtesy, Professor A. Müller, Bielefeld, W.G.

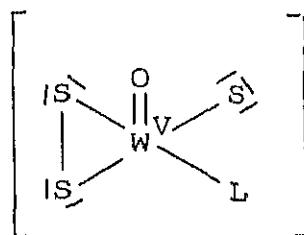
for MoS_4^{2-} is at 467 nm. This difference in absorption may be taken as a qualitative guideline to understand any difference in the reactivity of these thiometallates when electron transfer reactions are under consideration. Intramolecular electron transfer across W-S bond may be schematically shown as follows:



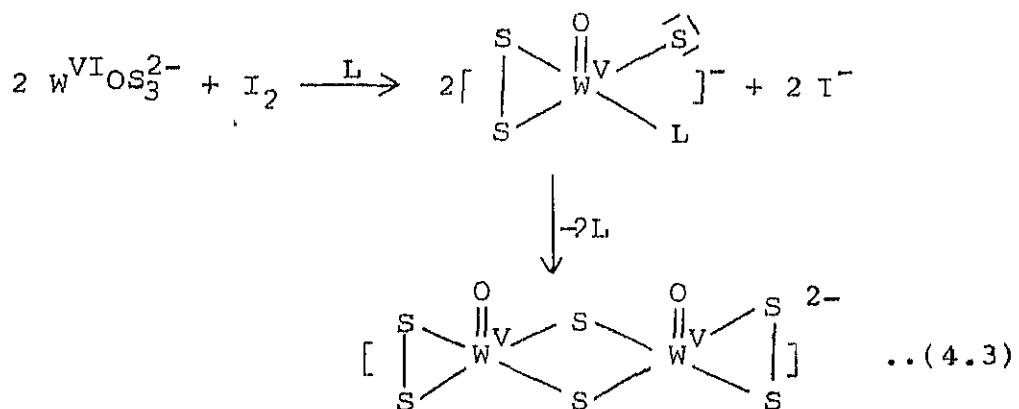
Structures (4.1a) and (4.1b) simply show the resonating forms of the tungsten sulfide attachment. The structure 4.1b is attained under the extreme reaction conditions imposed on the system. This could be achieved by several means (vide supra). This form is ready to interact with the external oxidant. Electrophilic attack by iodine might give the intermediate like $[W \begin{smallmatrix} S-I \\ S \end{smallmatrix}]$. The energy level of this intermediate could change in such a manner that the frontier orbitals related to tungsten and sulfur might come close in energy and the electron transfer from sulfur to tungsten followed by sulfur-sulfur bond formation might take place. The formation of disulfide is reminiscent of the reaction of iodine with RS^- to form $R-S-S-R$. The process can be viewed as follows:



If this happens to be the cause of the reaction occurring, an intermediate, monomeric, pentavalent tungsten species could be identified in the progress of the reaction, if not isolable. The intermediate pentavalent species arising from WOS_3^{2-} might have the structure:

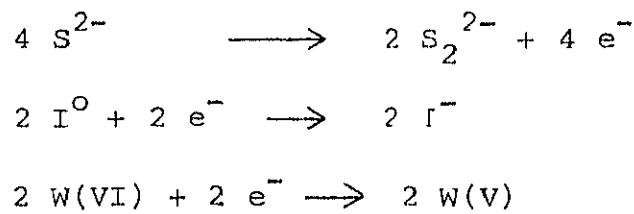


The coordination of the solvent (L) in this structure is in confirmation with the known stable pentavalent complexes of molybdenum and tungsten.^{113-116,129} The presence of an intermediate, monomeric species of this type has been shown by E.S.R. spectroscopy (vide infra). This species might dimerise to give the desired product as shown below:



Overall process involved is the 4e^- oxidation of 4S^{2-} coordinated to $\text{W}(\text{VI})$, and the formation of two S_2^{2-} ligands. Out of

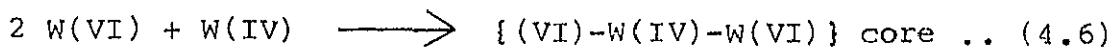
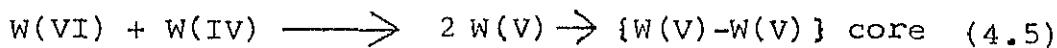
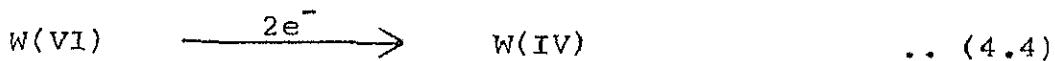
four electrons generated, the two go to external oxidant 2 I^0 to produce 2 I^- and the remaining two go, one each, to the two W(VI) (internal oxidant) to produce two W(V), as shown below:



Sometimes the rate of addition of the external oxidant, concentration of the reactants and the presence of counter ion govern the course of the reaction. Thus, the isolation of $[\text{W}^{\text{IV}}\text{S}(\text{W}^{\text{VI}}\text{S}_4)_2]^{2-}$ directly suggests that the generation of W(IV) species takes place directly presumably by the acceptance of two electrons by W(VI) center and the excess WS_4^{2-} functions as bidentate ligand, competing with any S_2^{2-} ligands formed in the reaction. Presence of bulky cation freezes the reaction at this point and the formation of trinuclear species is achieved. When two electron oxidants are used, both the products can be obtained depending upon the reaction conditions. There is no apparent difference in the inducing reactivity of the external oxidants Ph-S-S-Ph, $(\text{CH}_3)_3\text{COOH}$, or Ph- $\text{CH}_2-\text{O}-\text{O}-\text{CH}_2-\text{Ph}$. However, when persulfate $\text{S}_2\text{O}_8^{2-}$ is used, reaction takes place at low temperature.

As stated earlier, reaction time is also crucial in such systems, prolonging the reaction results in the formation of di-nuclear species having W(V) center. This suggests that the other possible electron transfer pathway could be similar to that of the

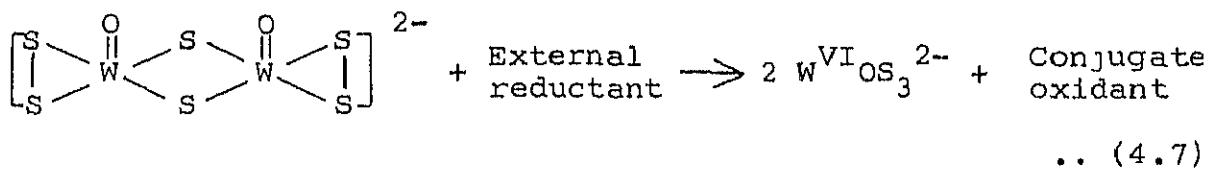
scheme proposed by Muller and later by Stiefel and coworkers^{36,40} in the synthesis of $[\text{Mo}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ and $[\text{M}^{\text{IV}}\text{S}(\text{M}^{\text{VI}}\text{S}_4)_2]^{2-}$, (M = Mo, W). The other possible scheme can be described as shown below:



The formation of $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ in aqueous medium using persulfate as an oxidizing agent shows the dependence of the reaction on the counter ion to determine the course of the reaction. If the bulky cation is not added in the beginning, along with $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ another species containing $\{\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2\}^{2+}$ core is obtained which has WS_4^{2-} instead of S_2^{2-} as bidentate ligands.¹³¹ Contrary to molybdenum system the reaction of WS_4^{2-} and persulfate does not yield $[\text{W}_3^{\text{IV}}(\text{S})(\text{S}_2)_6]^{2-}$ anion. This may be attributed to the instability of $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ in solution. Further reduction of W centers leads to the total decomposition of the complex.

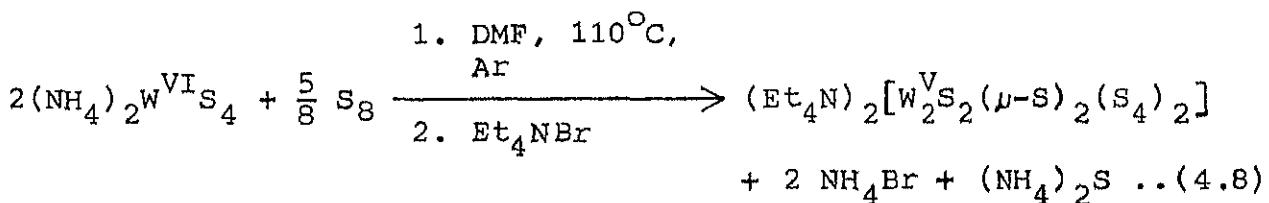
Interestingly, the reaction of $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ and methanolic polysulfide solution at ambient conditions produces $\text{W}^{\text{VI}}\text{OS}_3^{2-}$ which suggests the involvement of a complimentary reaction. Here an induced electron transfer process takes place in a reverse direction. Polysulfide, S_x^{2-} functions as an external

reductant and causes the electron transfer from metal, W(V) to coordinated ligand S_2^{2-} . Conversion of two S_2^{2-} to $4 S^{2-}$ requires four electrons. Two electrons are supplied by internal reductant $2 W(V)$ and the rest two electrons are supplied by external reductant S_x^{2-} . The nature of the reaction has been established as shown in Eqn. (4.7):



When a DMF solution of $[W_2^{V}O_2(\mu-S)_2(S_2)_2]^{2-}$ is treated with methanolic polysulfide solution, there is immediate drop in the extinction coefficient of the bands responsible for this core. If this mixture is slightly warmed, the reaction becomes faster and quantitative conversion of $[W_2^{V}O_2(\mu-S)_2(S_2)_2]^{2-}$ to WOS_3^{2-} is achieved.

The above mentioned complimentary reaction has also been observed by Stiefel and coworkers in the synthesis of $[W_2^{V}S_2(\mu-S)_2(S_4)_2]^{2-}$. The following reaction proceeds only under a strong jet of argon gas on the surface of the reaction mixture. If reaction conditions are not standardized W(VI) species are also obtained along with the product.



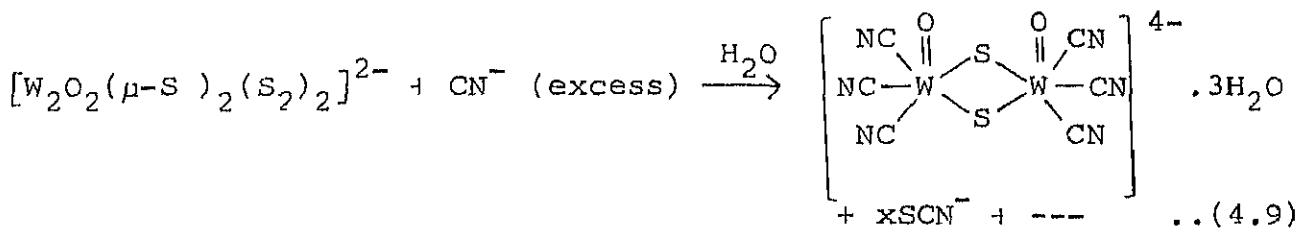
In this case one of the byproducts, $(\text{NH}_4)_2\text{S}$ might combine with elemental sulfur to form ammonium polysulfide which in turn might react with $[\text{W}_2^{\text{V}}\text{S}_2(\mu-\text{S})_2(\text{S}_4)_2]^{2-}$ in a complimentary fashion, pushing the equilibrium in the backward direction, thereby forming WS_4^{2-} . Thus, the role of the argon jet is to remove byproduct $(\text{NH}_4)_2\text{S}$ and to push the reaction in the forward direction.⁴⁸

Formation of MoS_9^{2-} from MoS_4^{2-} and elemental sulfur (external oxidant) is readily achieved whereas under similar reaction conditions WS_9^{2-} is not formed. This clearly shows the difference in reactivity between these two thiometallates, MoS_4^{2-} and WS_4^{2-} anions. However, molybdenum analog of $[\text{W}_2^{\text{V}}\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$ is formed under mild condition.⁴⁸ This suggests that the anion WS_9^{2-} might exist in solution if not isolable. This species has not been isolated so far, however, it has been shown by Coucouvanis and coworkers that MoS_9^{2-} reacts readily with activated acetylene to yield the tris-dithiolene chelate $[\text{Mo}^{\text{IV}}(\text{S}_2\text{C}_2^{2-})(\text{COOMe})_3]^{2-}$.⁷⁶ In this reaction the oxidation state of the central metal atom remains unchanged. Similar dithiolene complexes of Mo and W have been synthesized by Stiefel and coworkers where no apparent redox chemistry is involved. However, we have observed that the reaction between WS_4^{2-} and dibenzoyl acetylene in the presence of elemental sulfur yields, a tris-dithiolene complex anion $[\text{W}^{\text{IV}}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]^{2-}$. Same results were obtained when MoS_4^{2-} anion is used in place of WS_4^{2-} anion.¹³³ Thus, it may be inferred that WS_4^{2-} and elemental sulfur does give a reactive intermediate very much similar to MoS_9^{2-} which in turn reacts with the activated acetylene to

produce the monomeric tris-dithiolene complex of W(IV).

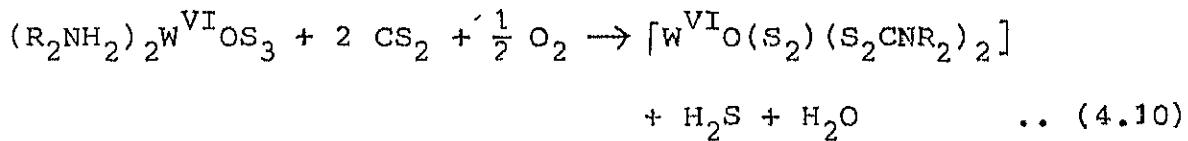
Recently, an interesting reaction between $[\text{Mo}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ and activated acetylene has been shown where insertion has taken place across Mo-S bond with the formation of vinyl dithiide group.⁷⁸ Coucovanis and coworkers in a series of reaction have shown that there is a distinct difference in the reactivity between S_2^{2-} and S_4^{2-} ligands coordinated to molybdenum systems.⁷⁹ They have suggested that sometimes insertion of the above type might take place at ambient temperature which on refluxing at higher temperature changes to stable dithiolene isomer.^{79,80} The reaction between $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S}_2)(\text{S}_2)_2]^{2-}$ and dibenzoyl acetylene (DBA) at room temperature gives the dithiolene product $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S}_2)_2(\text{S}_2\text{C}_2(\text{COPh})_2)_2]^{2-}$ instead of forming vinyl dithiide ligand as has been observed in the corresponding molybdenum analog. This reaction is expected from symmetry consideration contrary to molybdenum reaction.⁸⁰ However, the cleavage of S-S bond in coordinated S_2^{2-} even at ambient temperature is suggestive of instability of $\text{W}_2\begin{array}{c} \text{S} \\ \diagup \\ \diagdown \\ \text{S} \end{array}$ moiety compared to $\text{Mo}_2\begin{array}{c} \text{S} \\ \diagup \\ \diagdown \\ \text{S} \end{array}$ (vide infra).

The difference in reactivity between $[\text{Mo}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ and $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S}_2)(\text{S}_2)_2]^{2-}$ is further reflected in a reaction of these two anions with KCN. Contrary to molybdenum system¹³³ where reduction of molybdenum centers takes place, the tungsten system shows a simple substitution reaction with the formation of $[\text{W}_2^{\text{V}}\text{O}_2(\mu\text{-S})_2(\text{CN})_6]^{4-}$ as shown below:



The reactivity of $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$ has also been checked with CS_2 . No reaction takes place even on refluxing the two for hours.

The reaction between $(\text{R}_2\text{NH}_2)_2\text{WOS}_3$ and CS_2 in the presence of oxygen gives $[\text{W}^{\text{VI}}\text{O}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$. This reaction is actually an induced electron transfer reaction but paradoxically seems to be similar to a purely ligand redox process. The stoichiometry of this reaction has been established as shown in reaction (4.10).



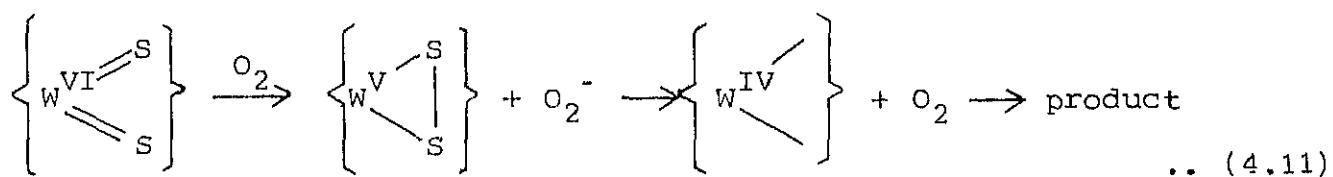
$\text{R}_2\text{NH} = \text{Et}_2\text{NH}, \text{Pr}_2\text{NH}, \text{C}_6\text{H}_5\text{NH}$.

The formation of $[\text{W}^{\text{VI}}\text{S}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2]$ can also be effected following the reaction (4.10) using the corresponding salt of tetrathiotungstate(VI). This product is similar to the one formed by reacting WS_4^{2-} and tetraalkylthiuram disulfide as

oxidant.¹³⁴ The difference lies in the type of reaction involved herein. The latter reaction is a purely ligand based redox process whereas reaction (4.10) involves the participation of tungsten.

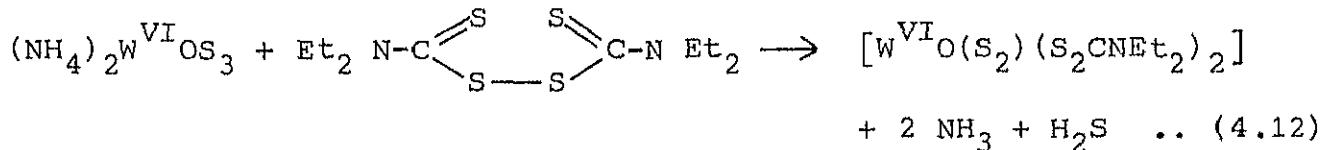
The product of the reaction (4.10) maintains hexavalent tungsten apparently suggesting a purely ligand redox reaction. The conversion of two S^{2-} ligands to one S_2^{2-} ligand and the uptake of two electrons by $\frac{1}{2} O_2$ as electron acceptor furnishes an electron balanced reaction. The participation of tungsten in this reaction is observed as an intermediate ESR active W(V) species formed during the course of the reaction (vide infra). The observed reactions do not take place if the reaction is carried out exclusively in an inert or H_2S atmosphere. This rules out the possibility of the involvement of H^+ as an alternative electron acceptor. The disappearance of the ESR active species after 20 hr might be due to (1) further reduction of W(V) to W(IV), (2) oxidation of W(V) to W(VI) or (3) dimerization of W(V). The third possibility can be ruled out as no dimeric W(V) compound could be isolated under the reaction conditions within 40 hr. Second possibility, i.e. the oxidation of W(V) to W(VI) should lead to the formation of the product. Freezing of the reaction at this stage gives the product in low yield (~30%). Thus to increase the formation of the product in more than two fold from this stage, the last 16 hr are crucial when the reaction mixture is ESR silent. This gives us an indirect credence to rely on the first possibility. This suggests that the electron transfer from

S^{2-} ligand to W(VI) takes place to make it W(IV) via a kinetically competent W(V) species. The electron transfer pathway can be described as shown in Eqn. (4.11).



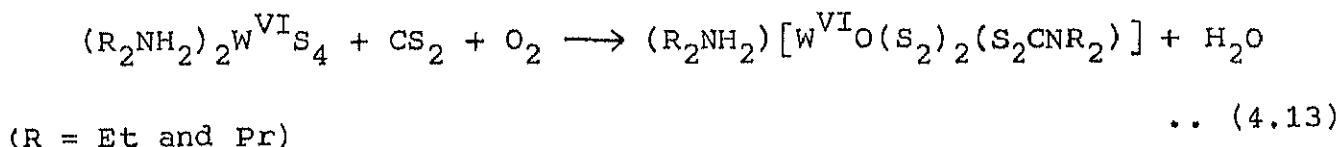
The above scheme where superoxide, O_2^- is generated, is verified by observing the conversion of benzyl bromide to benzyl alcohol.¹³⁵⁻¹³⁸ Formation of benzyl alcohol was checked by adding benzyl bromide into the reaction mixture and stirring it for 20 hr. The benzyl alcohol thus formed was extracted with diethyl ether and identified by GC using the column AC-30. Thus, both internal and external oxidants share one electron each donated by two S^{2-} with the formation of one S_2^{2-} . The formation of W(IV) is then resulted by the reduction of W(V) by O_2^- . The last step i.e. the oxidation of W(IV) to the product is achieved by aerial oxygen. The entire process of this ligand to metal electron flow is controlled by external oxidant, oxygen, functioning as terminal electron acceptor. The role of tungsten is to function as an electron sink.

The product $[\text{W}^{\text{VI}}\text{OS}_2(\text{S}_2\text{CNET}_2)_2]$ has also been achieved by reacting WOS_3^{2-} with tetraethyl thiuram disulfide at ambient temperature as shown below:

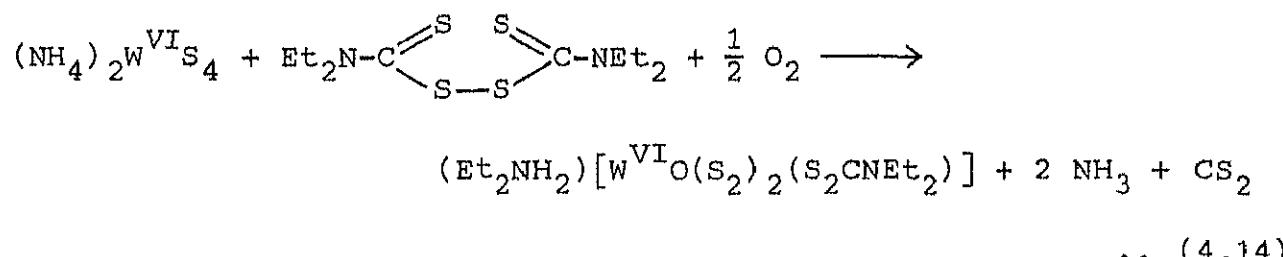


In this reaction there is no involvement of the metal center. The molybdenum analog of this compound is well known and has been synthesized by several different procedures.^{42,63,94} But none of these methods work in case of tungsten.

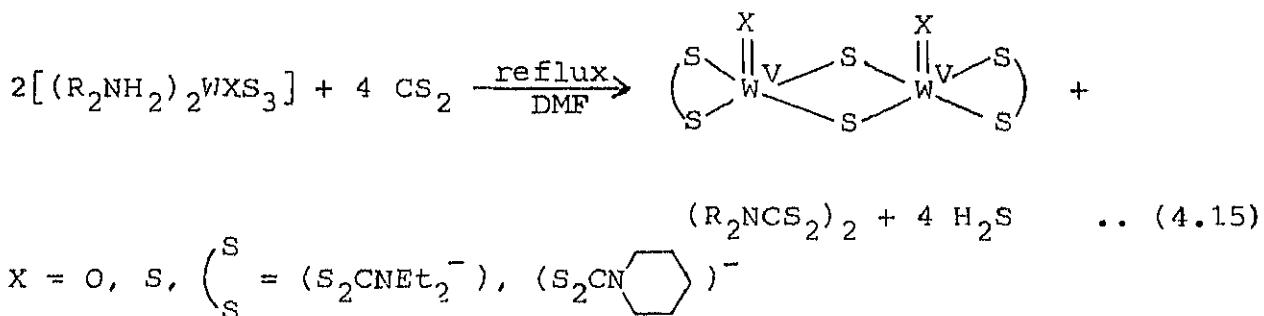
Similar reaction with less amount of CS_2 in the presence of oxygen leads to the conversion of $(\text{R}_2\text{NH}_2)_2\text{WS}_4$ to $(\text{R}_2\text{NH}_2)[\text{W}^{\text{VI}}\text{O}(\text{S}_2)_2(\text{S}_2\text{CNR}_2)]$. Though CS_2 was added more than the stoichiometric ratio to convert both the secondary amines to $(\text{S}_2\text{CNR}_2)^-$, yet the conversion of only one mole of amine to $(\text{S}_2\text{CNR}_2)^-$ is surprising and in fact leads to the stepwise formation of $(\text{S}_2\text{CNR}_2)^-$ even in the preparation of $[\text{W}^{\text{VI}}\text{O}(\text{S}_2)_2(\text{S}_2\text{CNR}_2)_2]$ (Reaction 4.10) (vide supra). The reaction is analogous to earlier one and the involvement of intermediate ESR active $\text{W}(\text{V})$ along with the generation of O_2^- suggests a very similar induced electron transfer reaction concealed under purely ligand based reaction:



The product $(\text{Et}_2\text{NH}_2)[\text{W}^{\text{VI}}\text{O}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)]$ has also been achieved by reacting WS_4^{2-} and tetraethylthiuram disulfide in the presence of oxygen at high temperature. This is a complicated ligand based redox reaction followed by decomposition of $\text{S}_2\text{CNET}_2^-$.

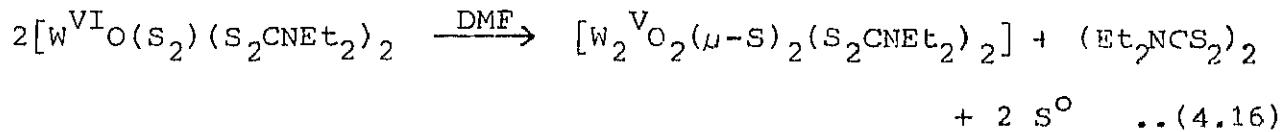


Tungsten(V)-sulfur complexes have generally been prepared by multi-step synthesis.^{48,139,140} A new method for their efficient one-step synthesis has been developed. Gradual heating of diethylaminium and piperidinium thiotungstates (WOS_3^{2-} , WS_4^{2-}) with excess CS_2 in DMF affords desired compounds, with the overall reaction as shown in Eqn. (4.15):



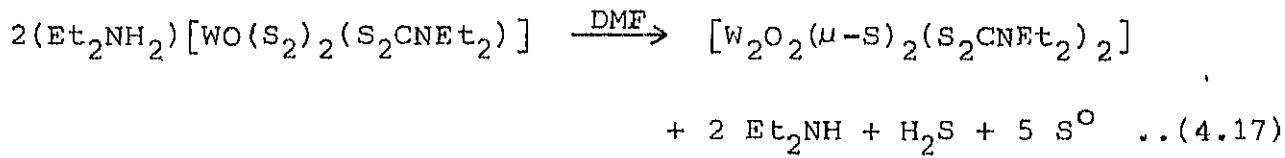
The formation of H_2S and thiuram disulfide as byproducts of the reaction establishes the stoichiometry of the reaction. The formation of thiuram disulfide is confirmed by comparison with an authentic sample (tlc). In the synthesis of $W_2V_2S_2(\mu-S)_2$ (S_2CNR_2)₂, compound $W_2V_2OS(\mu-S)_2(S_2CNR_2)_2$ is formed as byproduct by the hydrolysis of $W_2S_2(\mu-S)_2(S_2CNR_2)_2$ with the traces of moisture present in the reaction medium. The characterization of thiuram disulfide as a byproduct shows that it is a thermally induced redox reaction. Same reactants on prolonged stirring in air produce $[WOS_2(S_2CNR_2)_2]$ in good yield involving induced internal electron transfer process using aerial oxygen as external oxidant (vide supra). This compound on heating in DMF gives the dinuclear compound in good yield. The nature of this reaction

(Eqn. 4.16) has been established as shown below:

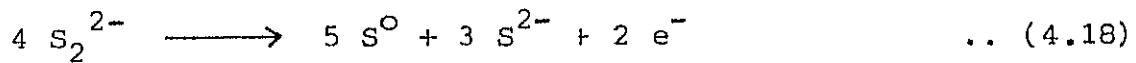


This reaction accounts for the reduction of two W(VI) of $[W^{VI}O(s_2)(s_2CNET_2)_2]$ to form W(V) dimer with the oxidation of two $(Et_2NCS_2)^-$ to give one tetraethylthiuram disulfide. The formation of elemental sulfur could be accounted for through thermal cleavage of S_2^{2-} to S^{2-} and S^0 . Thus the reaction (Eqn. 4.17) can best be described as thermally induced internal electron transfer reaction. Under vigorous reaction conditions and even by photochemical irradiation similar disproportionation reaction is envisaged.^{31,32}

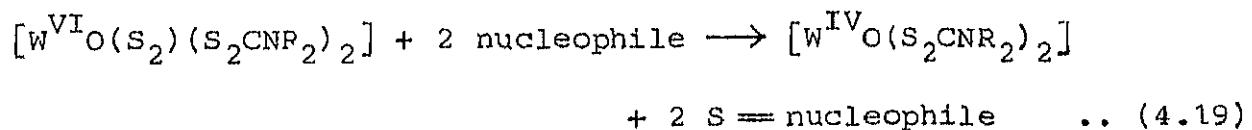
Another example of this type of reaction where $(Et_2NH_2)[WO(s_2)_2(s_2CNET_2)]$ in solution (DMF or DMSO) at room temperature slowly changes to the dinuclear compound is shown in the following Equation (4.17):



Here the coordinated S_2^{2-} ligands do not simply cleave to produce S^{2-} and S^0 but also induce the reduction of W(VI) to yield W(V) dimer. The overall reaction for S_2^{2-} ligand is a disproportionation reaction to supply the necessary electrons to reduce the metal centers further.



The reaction of $(\text{NH}_4)_2\text{WS}_4$ & $(\text{Et}_2\text{NCS}_2)_2$ gives $[\text{W}_2\text{S}_2(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$ in low yield. The low yield may be due to the formation of $(\text{NH}_4)_2\text{S}_x$ as a byproduct which combines with sulfur to give polysulfide. Polysulfide acts as an external reductant and oxidizes the product back to W(VI). However, the yield of product can be improved if a strong jet of argon is used over the surface of the reaction mixture to flush and the S_x^{2-} formed. The S_2^{2-} ligand in $[\text{W}^{\text{VI}}\text{O}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2]$, reacts readily with nucleophiles resulting in a sulfur transfer reaction, producing sulfur substituted nucleophile and a product $[\text{W}^{\text{IV}}\text{O}(\text{S}_2\text{CNR}_2)_2]$ with reduced metal center. The nucleophiles react with persulfido ligand of the complex in a straightforward pathway. the S-S and W-S bonds are cleaved and sulfur atom transfer to the nucleophile is effected (Eqn. 4.19):



The substituted nucleophiles have been identified by IR and chemical analysis.

Another interesting reaction is the regeneration of W(VI) complex. When the complex $[\text{W}^{\text{IV}}\text{O}(\text{S}_2\text{CNR}_2)_2]$ is treated with elemental sulfur, the coordinatively unsaturated W(IV) species undergoes the expected oxidative addition reaction. Conversion of 2 S^0 to S_2^{2-} and W(IV) to W(VI) furnishes the electron balanced

reaction. Similar observations in analogous molybdenum systems, have also been reported.^{63,141} The only difference lies in the fact that the tungsten analogs are more stable.

4.2 Structural Aspects of the Synthesized Complexes

4.2.1 Infrared Spectra

Infrared spectroscopy can reasonably determine the structural aspects of the synthesized complexes. For S_2^{2-} coordinated complexes, the identification of $\nu(S-S)$ mode of vibration is relatively an easy task. This is because of the fact that the $\nu(S-S)$ mode of vibration for S_2^{2-} is a strong one and normally appears in the region $480 - 600 \text{ cm}^{-1}$.⁶⁹ However, the situation becomes complicated when in addition to S_2^{2-} chelating ligand, the compound contains a terminal sulfido group, $\nu(W-S_t)$, which appears in the range 490 to 550 cm^{-1} (vide infra, Table 1.1). Thus, the identification of both the functional groups present together in the same compound may raise problems. The exact position of $\nu(W-S_t)$ mode of vibration is dependent upon the oxidation state of tungsten and the geometry of the complex. Distinction between these two modes of vibrations can be made readily if the oxo analog of the sulfido complex can be synthesized. In the case of oxo analog of this compound, the region $480-600 \text{ cm}^{-1}$ should show the presence of only $\nu(S-S)$ vibration. A comparison of this mode of vibration with that of the corresponding sulfur analog of the compound can thus help to resolve

the two vibrations related to $\nu(S-S)$ and $\nu(W-S_t)$ in this type of complexes.

The infrared spectra of the synthesized complexes containing these ligands are reproduced in Figs. 4.1.10 to 4.1.17. The comparison can be best represented by taking $[WO(S_2)(S_2CNET_2)_2]$ and $[WS(S_2)(S_2CNET_2)_2]$. In the former case a very strong absorption at 940 cm^{-1} can be readily assigned to $\nu(W=O)$ by comparing its spectrum with that of the reported molybdenum analog, $[MoO(S_2)-(S_2CNET_2)_2]$.^{94,141} The complex, $[MoO(S_2)(S_2CNET_2)_2]$ shows $\nu(Mo=O)$ around 915 cm^{-1} which on resolution shows splitting at 908 cm^{-1} and 920 cm^{-1} . However, the corresponding complexes with other dithiocarbamates show only one strong absorption responsible for $\nu(Mo=O)$ in this region.¹⁴¹ Recently, it has been observed that the solution spectrum of $[MoO(S_2)(S_2CNET_2)_2]$ shows a single absorption at 920 cm^{-1} assignable to $\nu(Mo=O)$.¹⁴² Splitting of this band is then probably due to solid state effect. In the tungsten complexes $\nu(W=O)$ appears around 940 cm^{-1} which is slightly higher than $\nu(Mo=O)$ observed in the corresponding molybdenum analogs. This suggests the involvement of stronger multiple bonding between tungsten and oxygen compared to molybdenum and oxygen. In all these tungsten complexes a band around 550 cm^{-1} of medium to strong intensity is assignable to $\nu(S-S)$ by comparing these with the corresponding molybdenum systems. It is to be noted that $\nu(S-S)$ vibration remains almost unaffected in the hepta-coordinated complexes of W(VI) and Mo(VI). On the

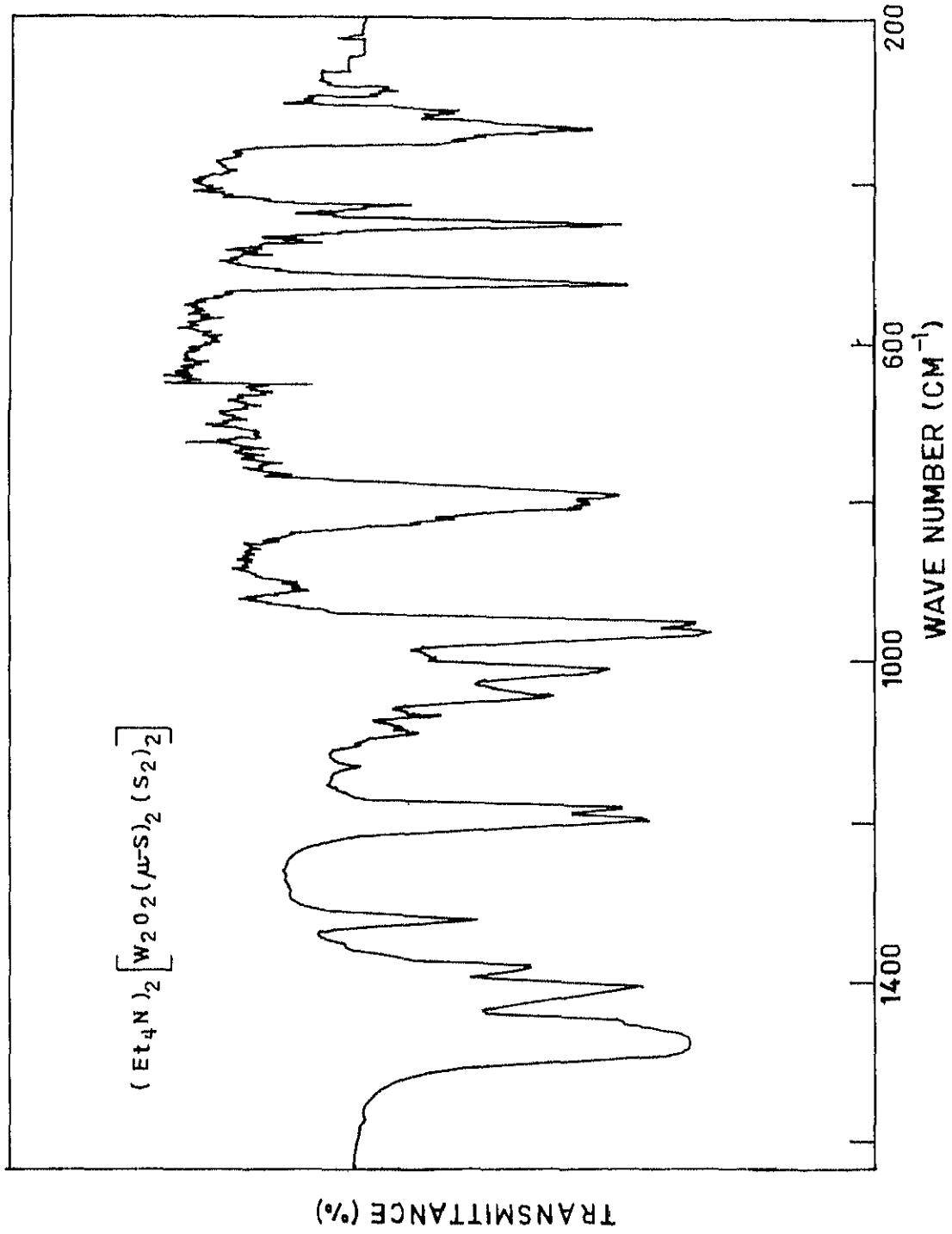


FIG. 4.1.1 INFRARED SPECTRUM

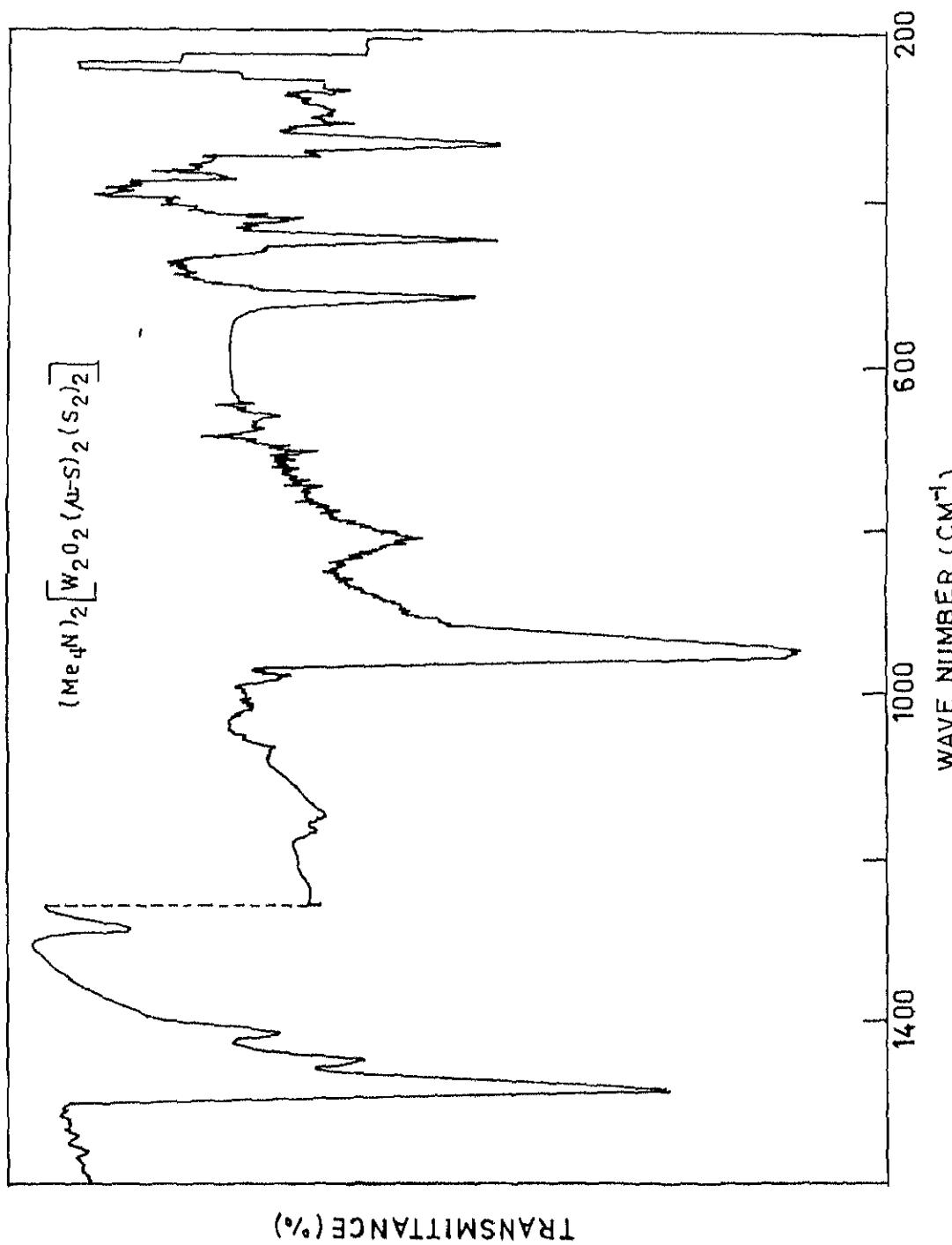


FIG 4.1.2 INFRARED SPECTRUM

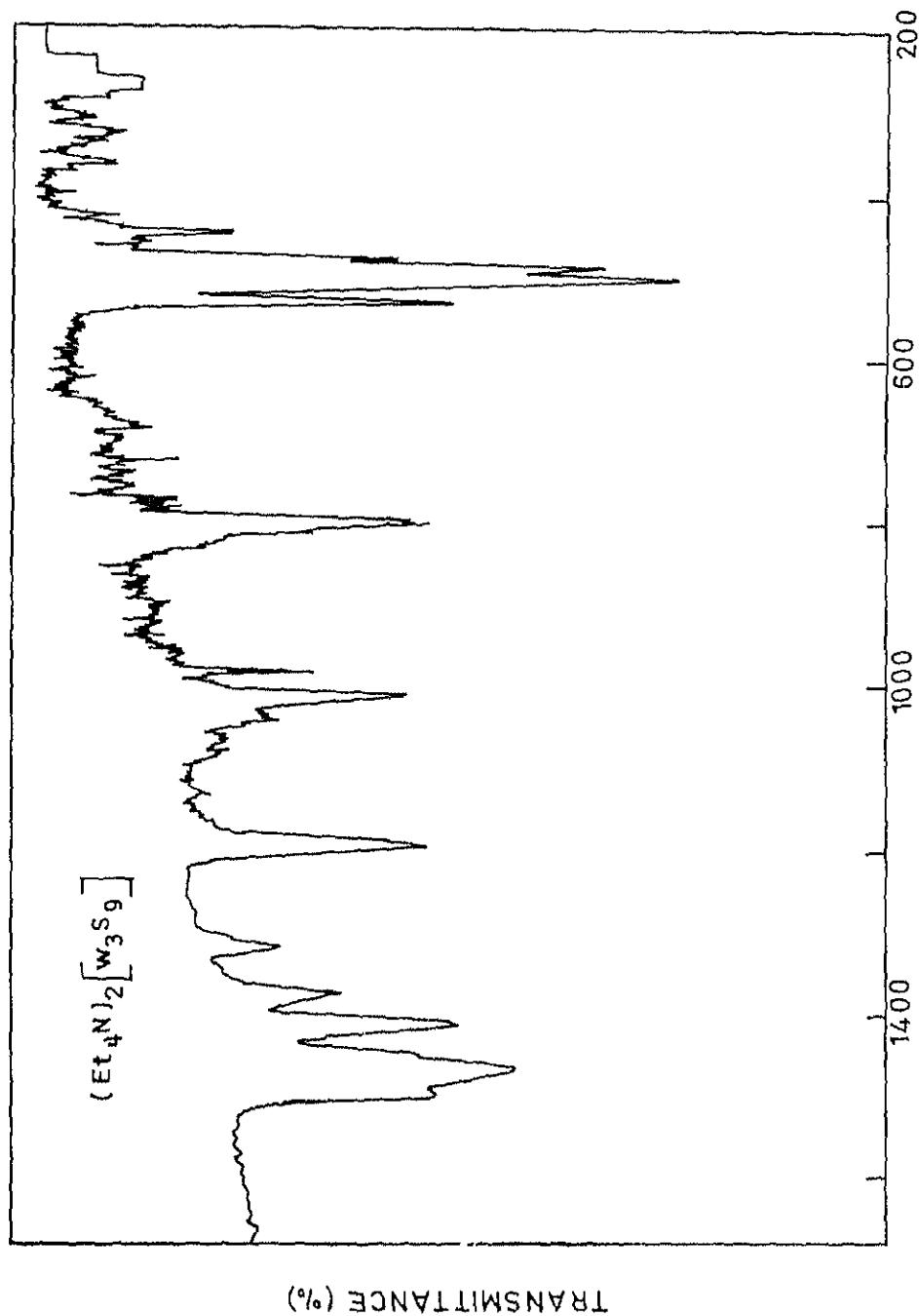
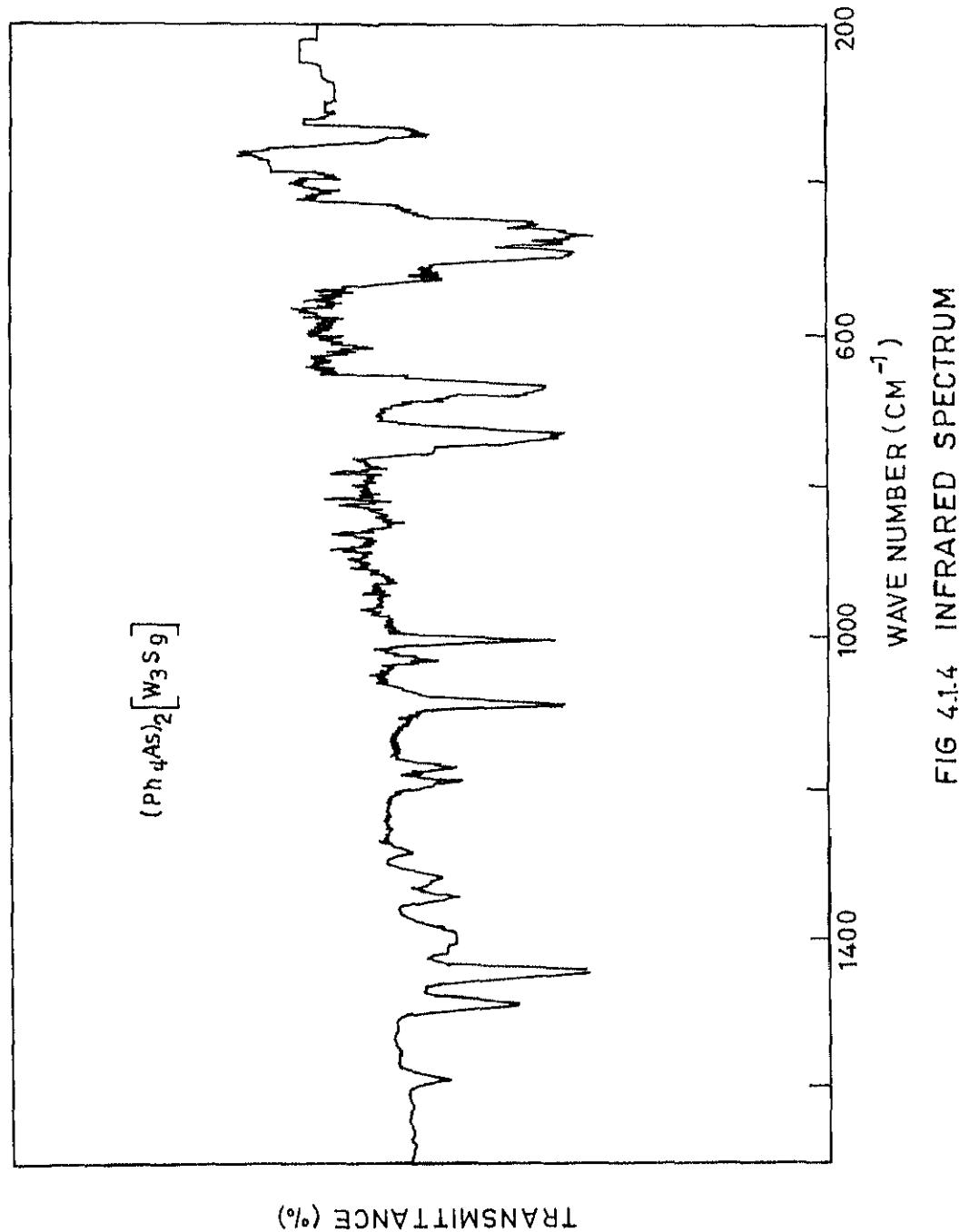


FIG. 4.1.3 INFRARED SPECTRUM



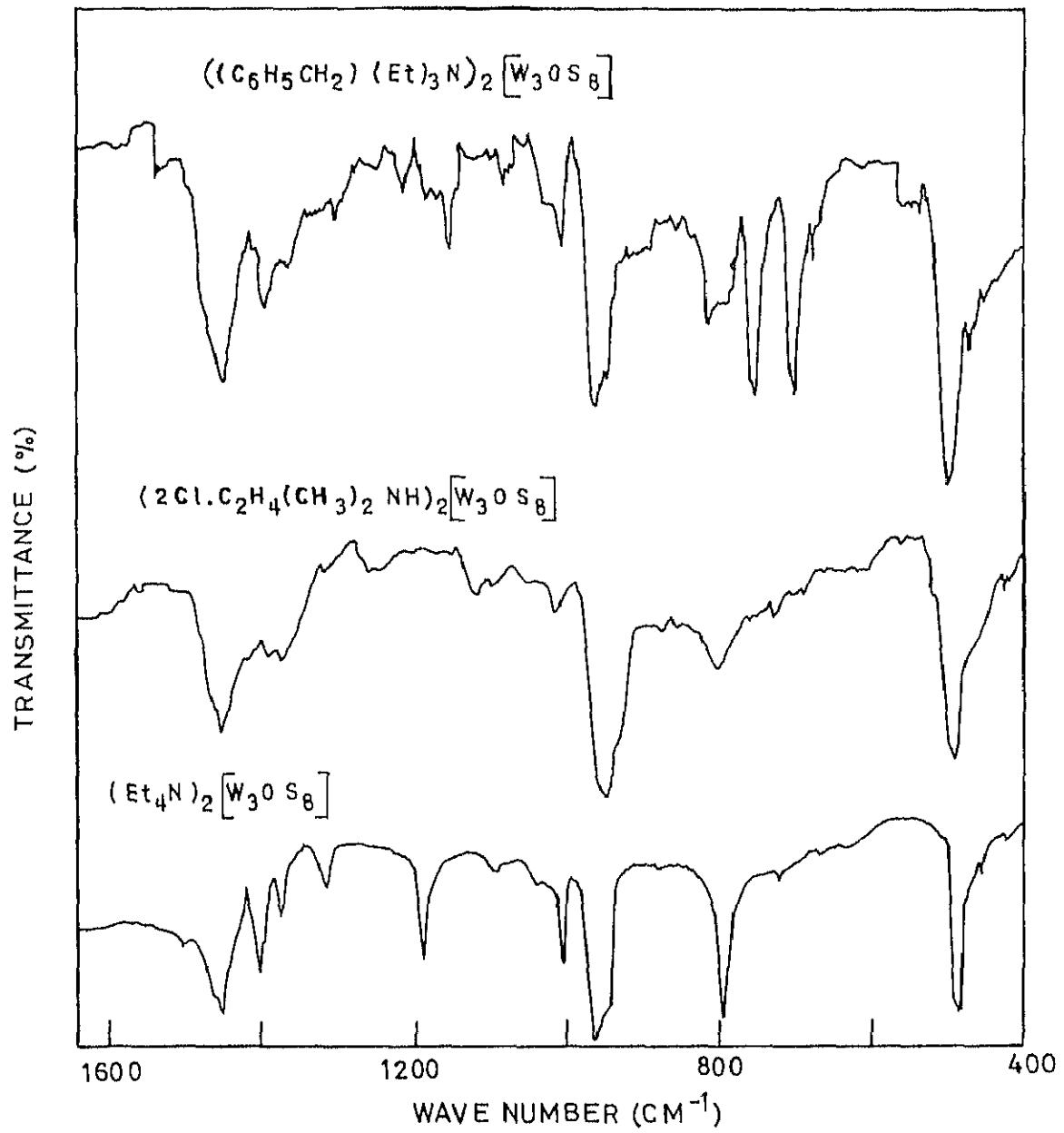


FIG. 4.1.5 INFRARED SPECTRA

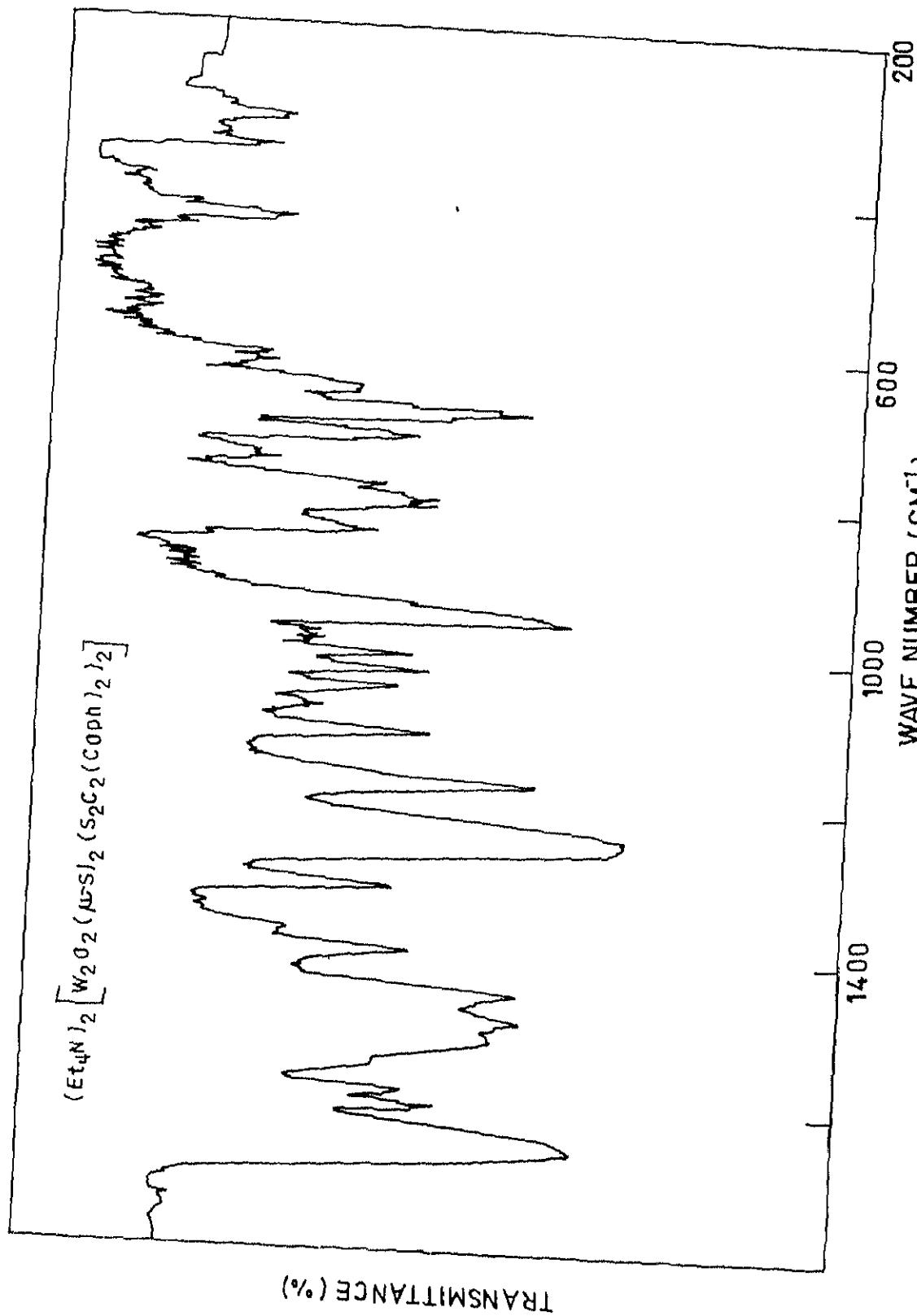


FIG. 4.1.6 INFRARED SPECTRUM

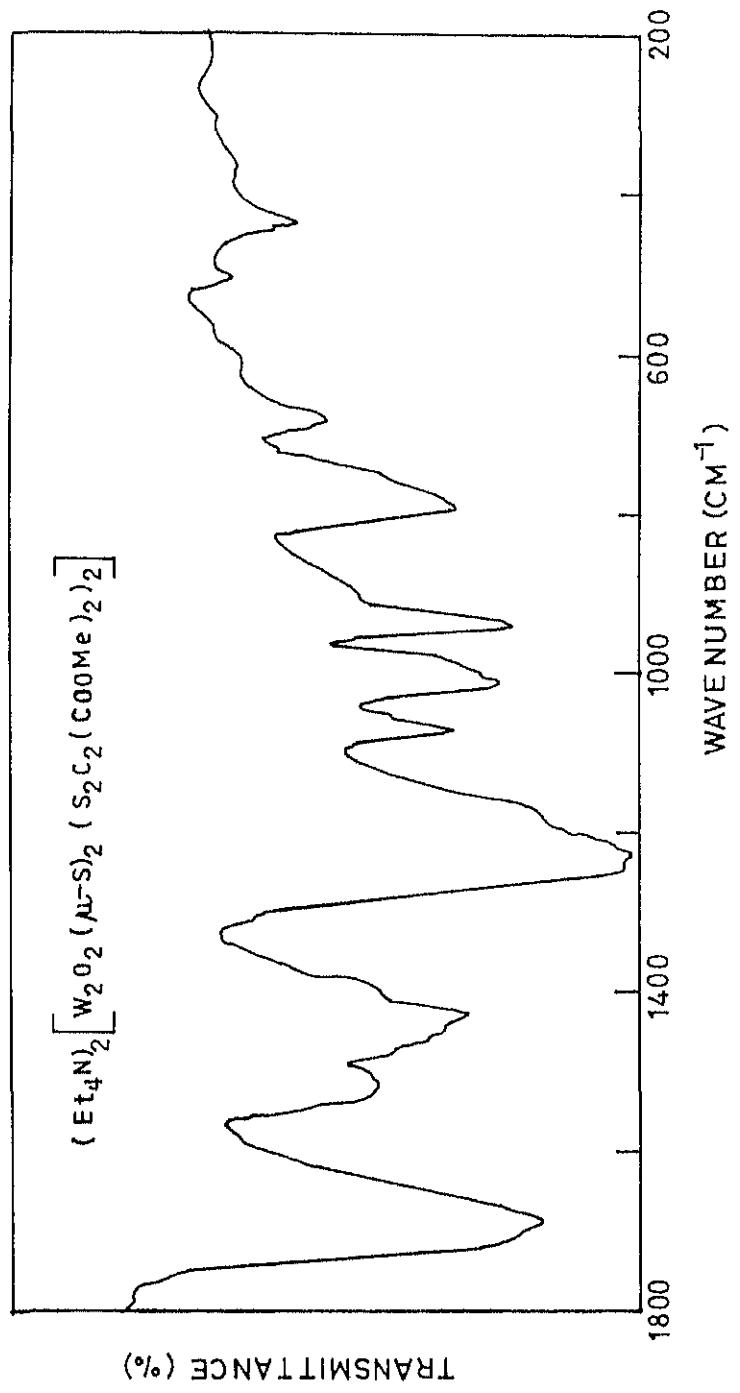


FIG 417 INFRARED SPECTRUM

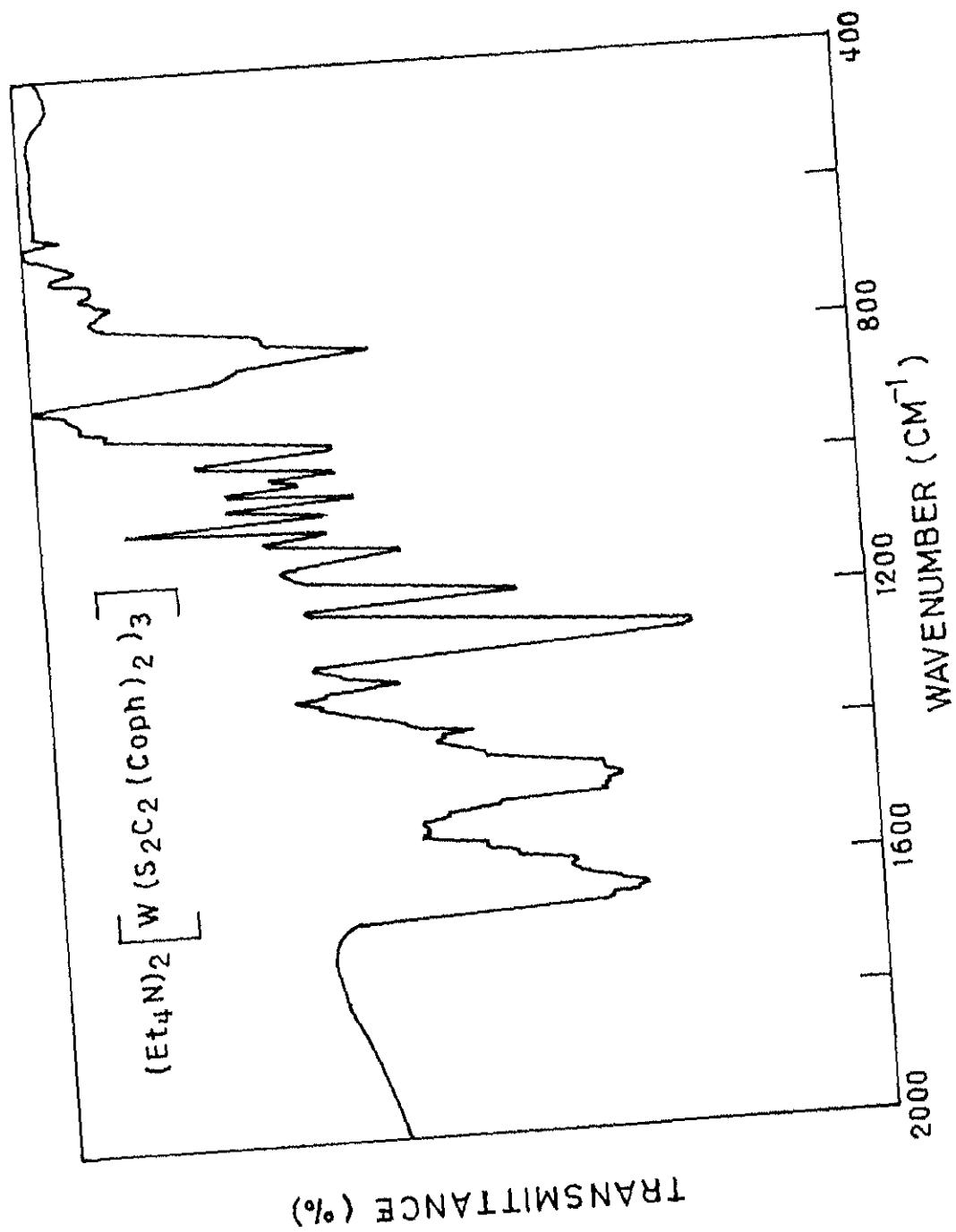


FIG. 4.1.8 INFRARED SPECTRA

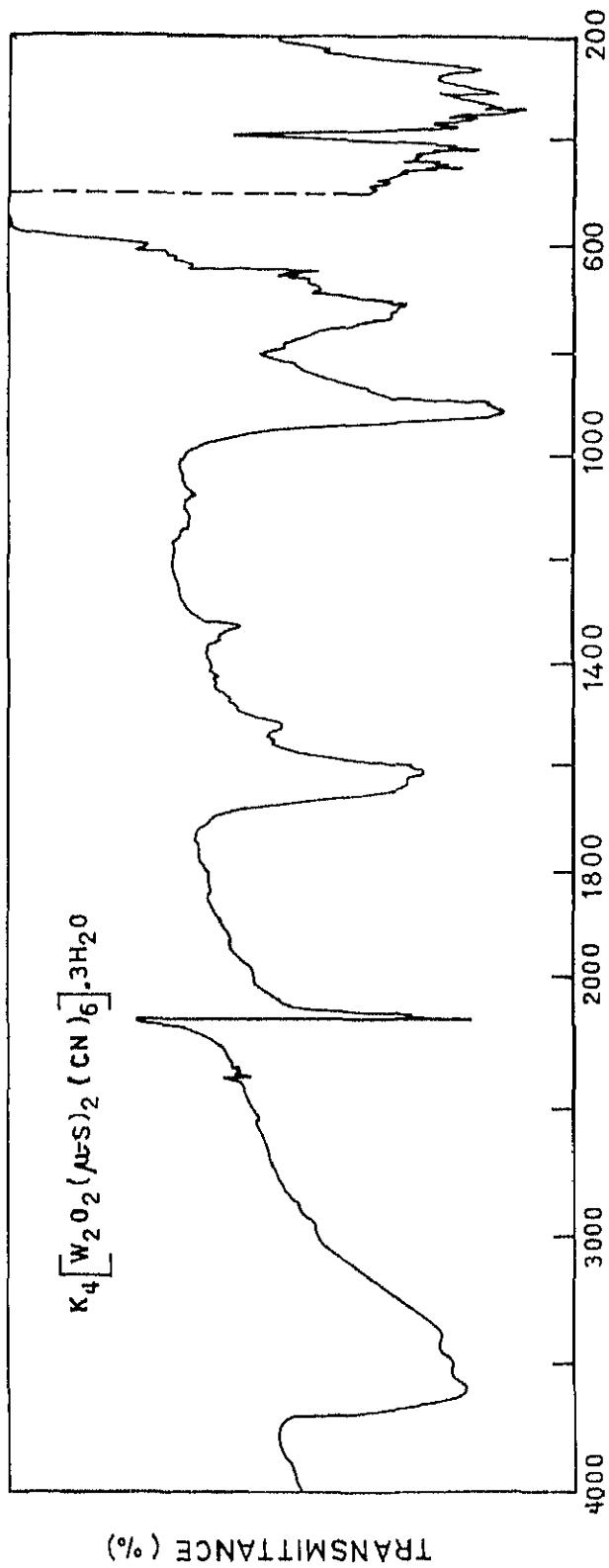


FIG 4.1.9 INFRARED SPECTRUM

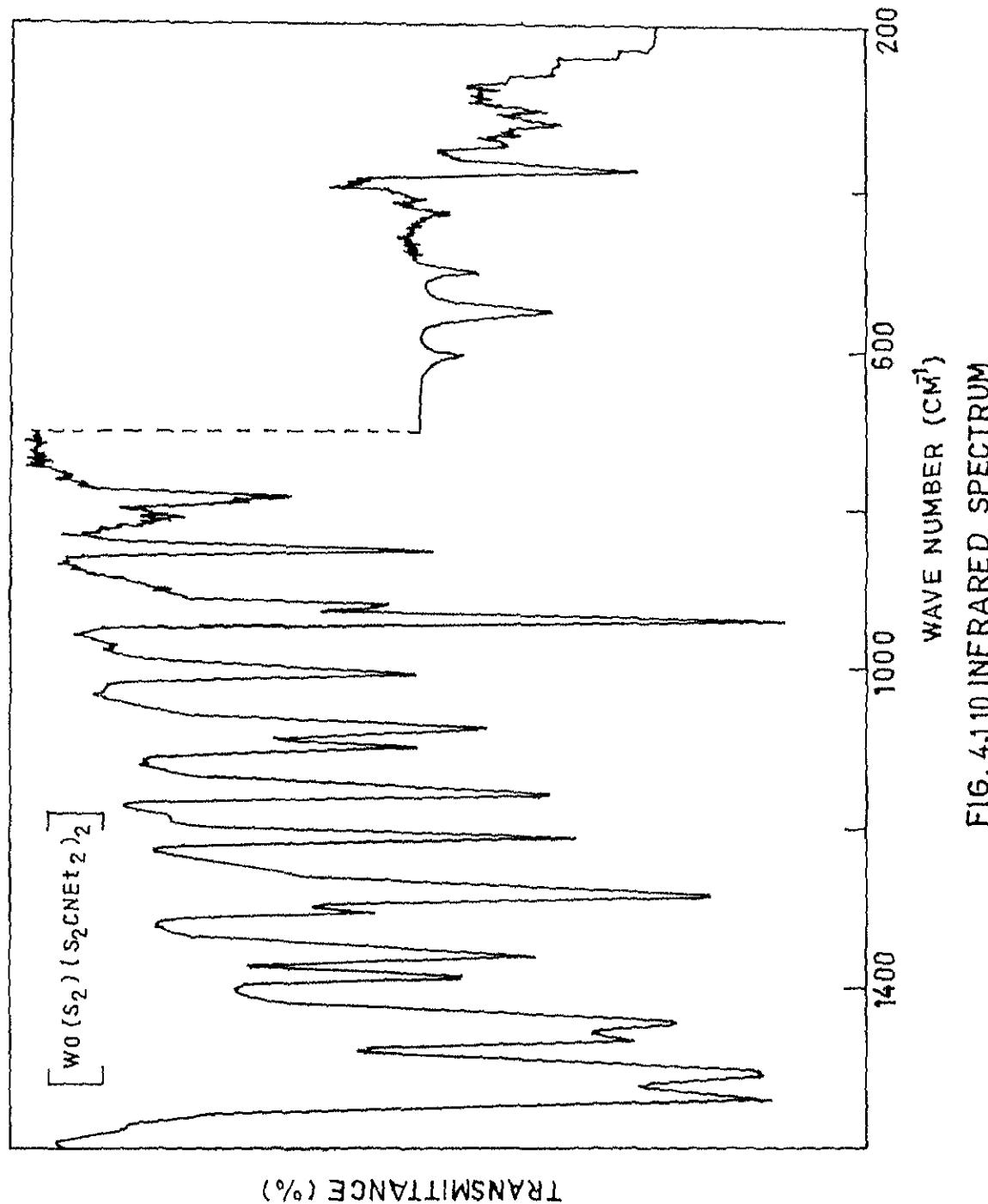


FIG. 4.110 INFRARED SPECTRUM

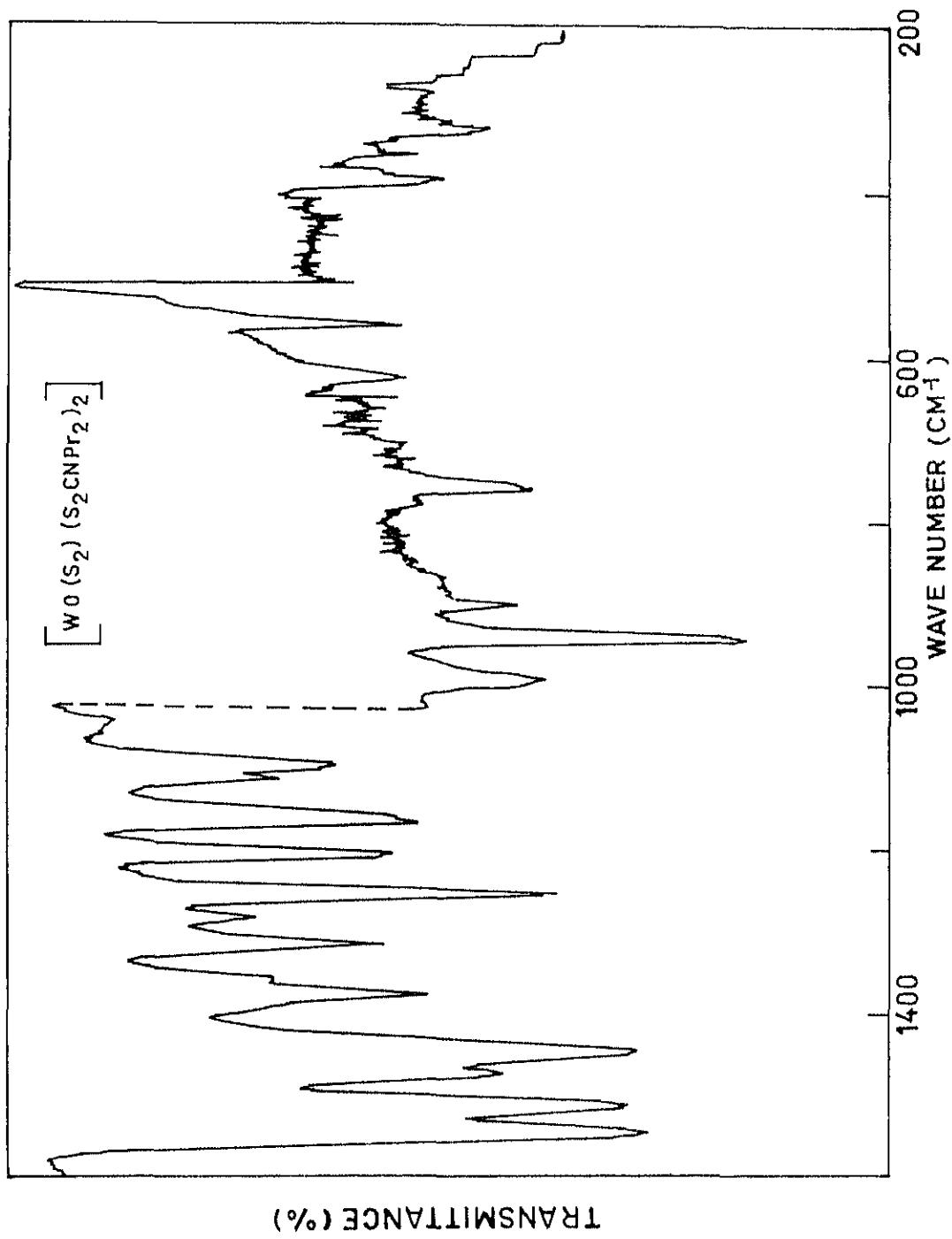


FIG. 4.111 INFRARED SPECTRUM

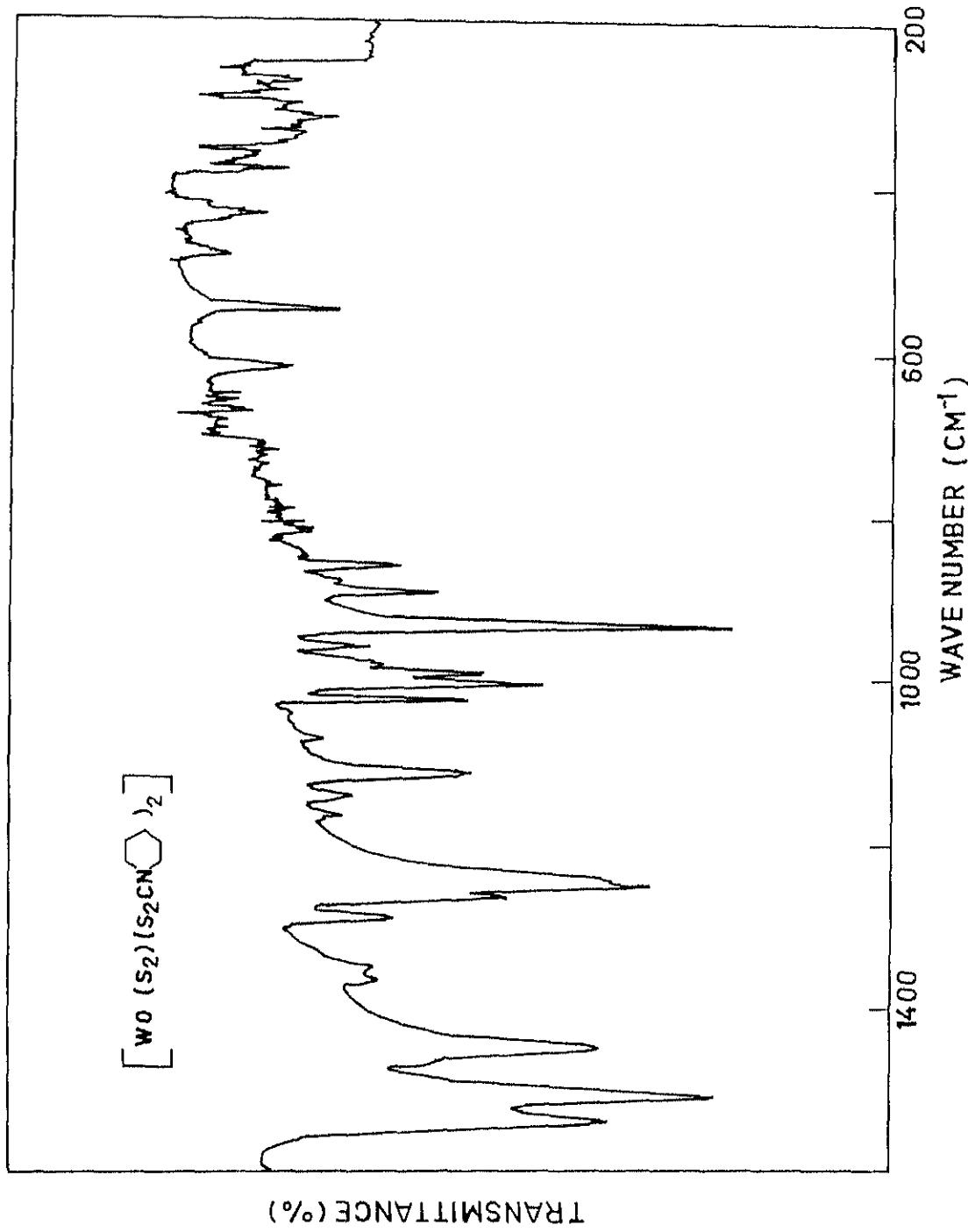


FIG 4.112 INFRARED SPECTRUM

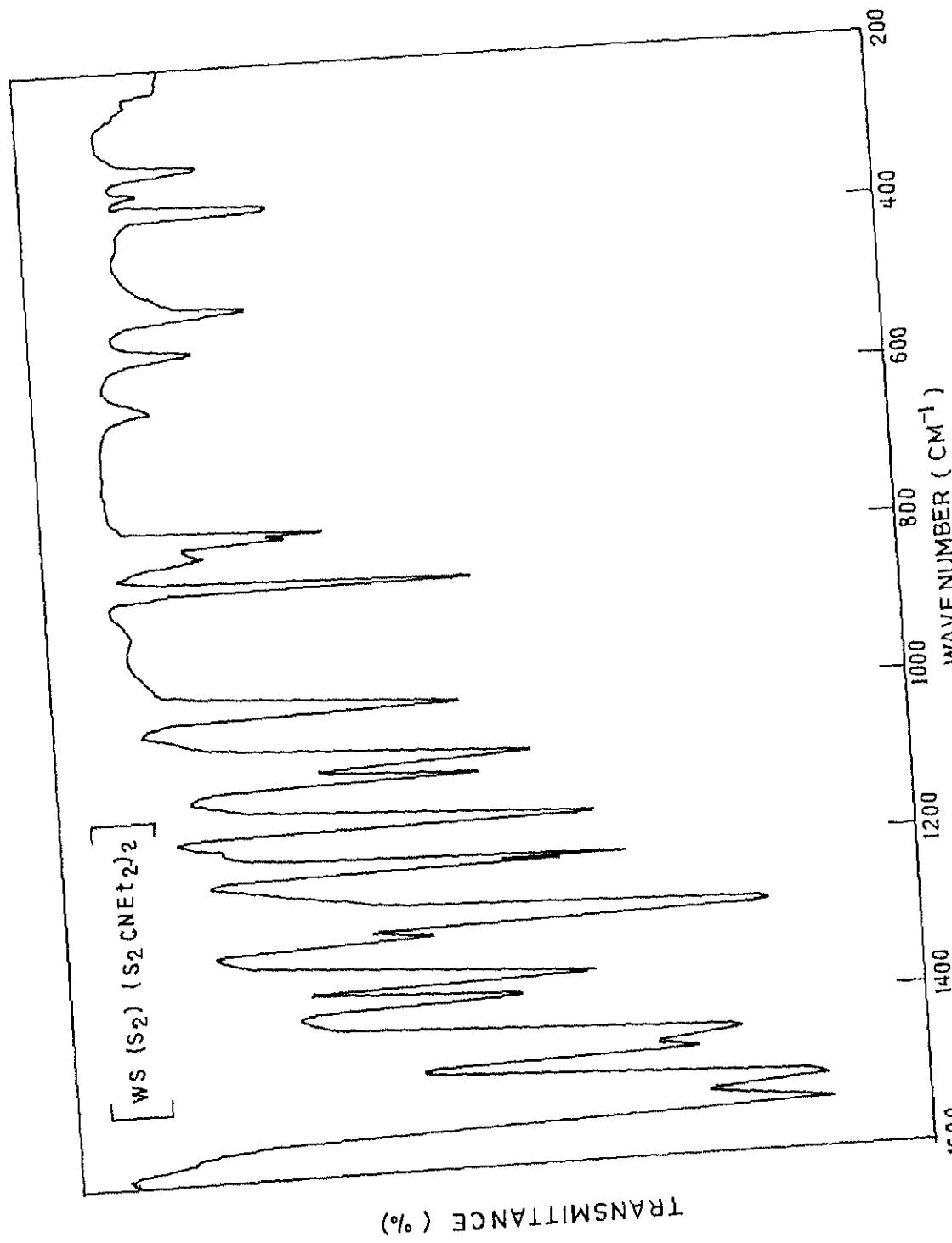


FIG. 4.1.13 INFRARED SPECTRUM

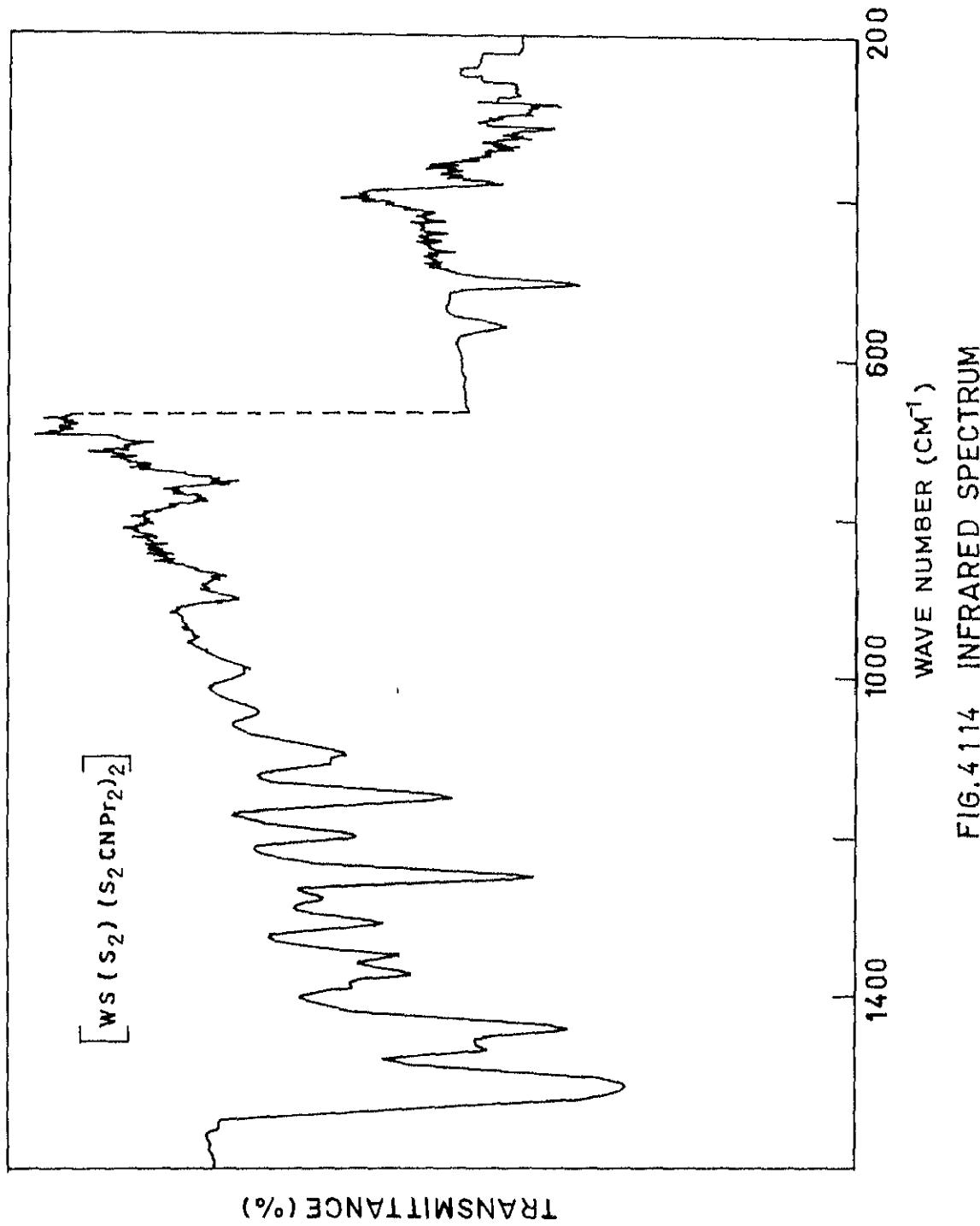


FIG. 4114 INFRARED SPECTRUM

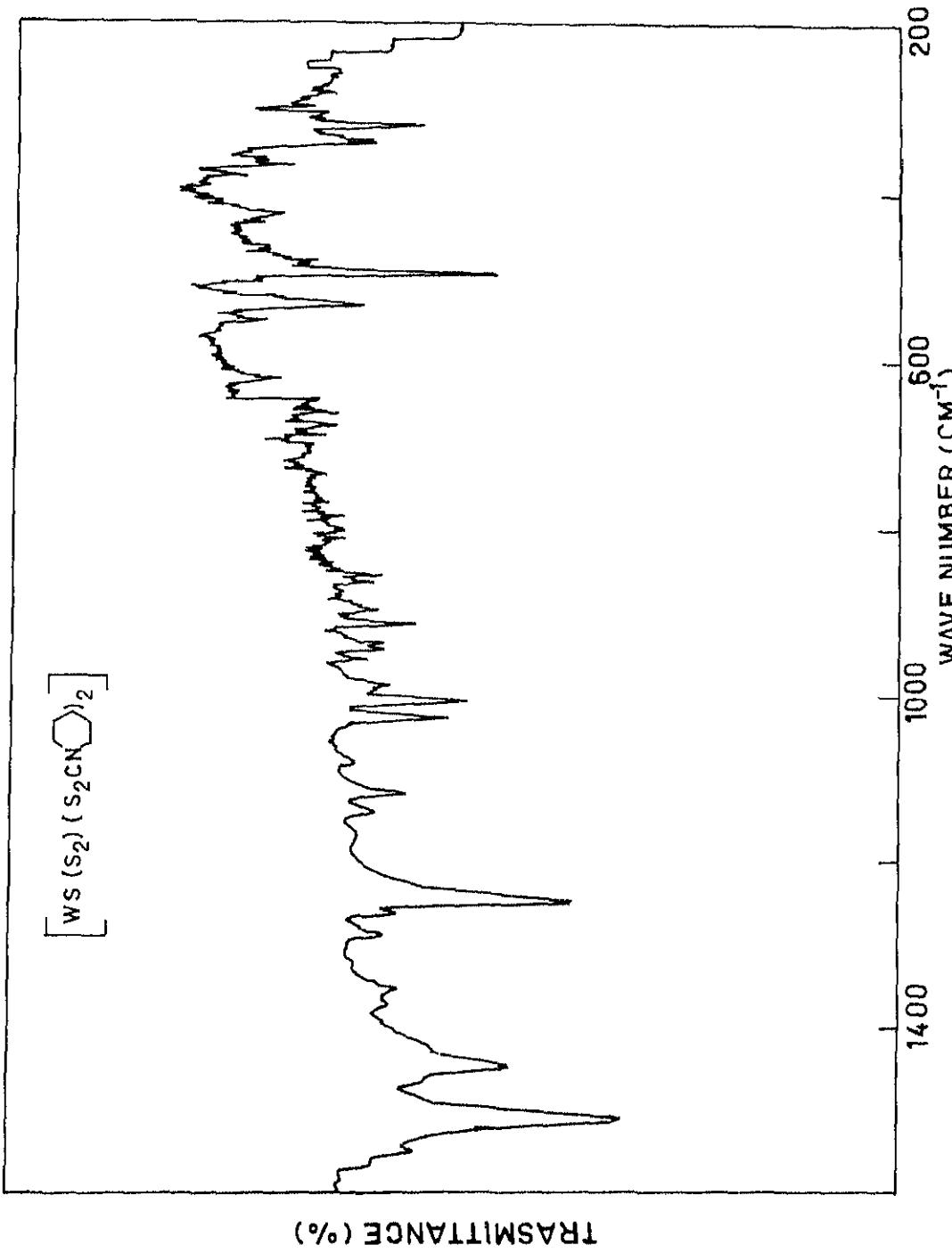


FIG. 4.1.15 INFRARED SPECTRUM

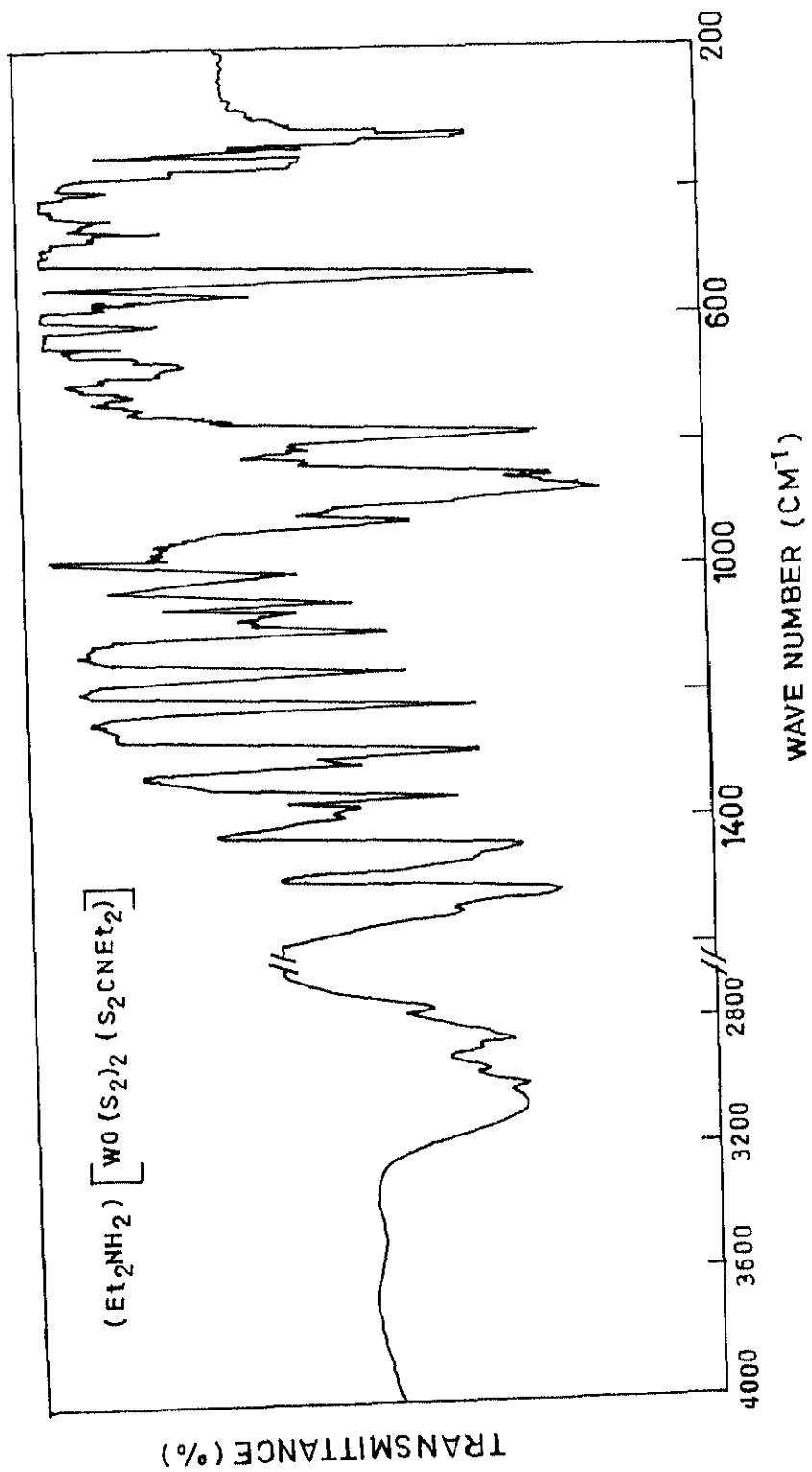


FIG. 4116 INFRARED SPECTRUM

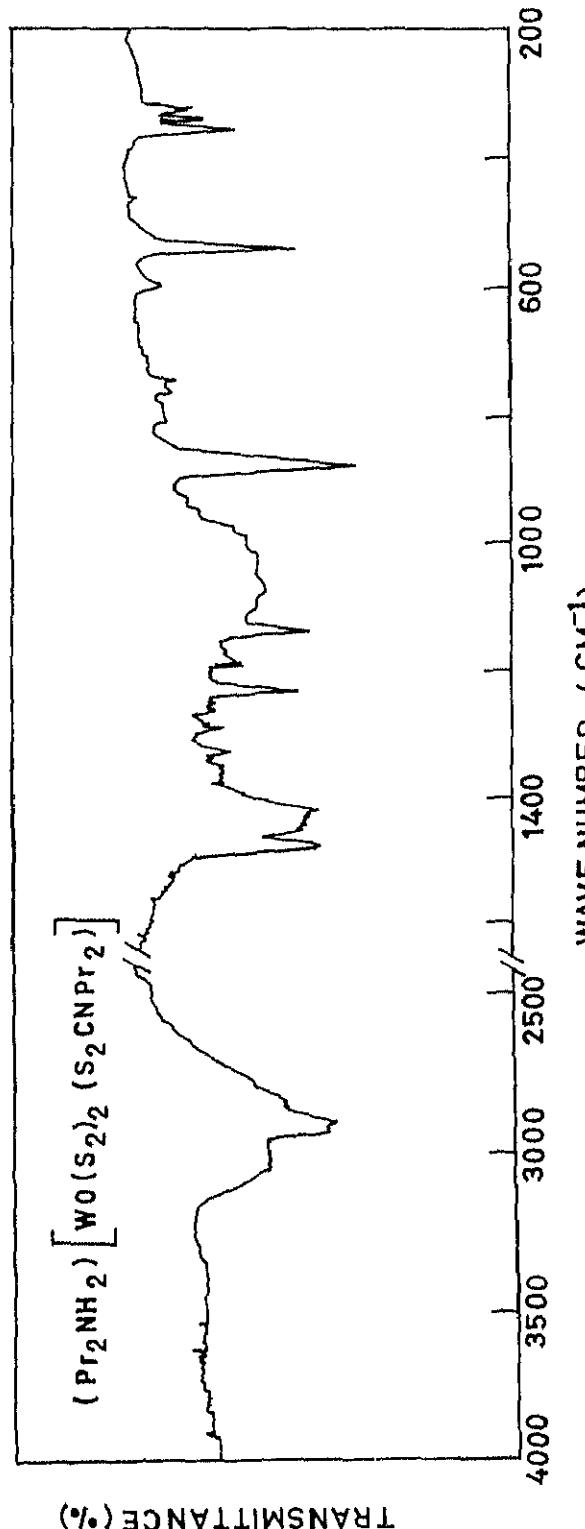


FIG. 4117 INFRARED SPECTRUM

basis of these observations one can now assign $\nu(W-S_t)$ in the series of all sulfur compound like $[WS(S_2)(S_2CNET_2)_2]$. The IR spectra of this class of compounds are reported in Figs. 4.1.13 to 4.1.15. The band appearing at 500 cm^{-1} is then assigned to $\nu(W-S_t)$ and the appearance of another band in the range of 535 to 550 cm^{-1} is then responsible for $\nu(S-S)$ vibration. This assignment is in good agreement with the data reported by Stiefel and coworkers⁴² for the corresponding $(S_2CNR_2)^-$ ligated compound. Identification of $\nu(W-S_2)$ is a difficult task because of the presence of thiocarbamate in the compound. When S_2^{2-} is coordinating in a side on fashion, the local symmetry of $\{W\begin{smallmatrix} S \\ | \\ S \end{smallmatrix}\}$ is C_{2v} , for which the expected normal mode of vibrations, are $\nu(S-S)$ (A_1), ν_s , $\nu(W-S)$, (A_1) of $\{W\begin{smallmatrix} S \\ | \\ S \end{smallmatrix}\}$ moiety and ν_{as} , $\nu(W-S)$, (B_1) of $\{W\begin{smallmatrix} S \\ | \\ S \end{smallmatrix}\}$ moiety, respectively. All these vibrations are IR active. The exact identification of the ν_s and ν_{as} vibrations would be difficult because of the presence of other vibrations arising from dithiocarbamate coordinated to tungsten as well as the possibility of strong coupling of A_1 mode of vibration with that of $\nu(S-S)$. The vibrations due to the presence of other ligand can be to some extent identified by comparing the infrared spectrum of $[WO(S_2CNR_2)_2]$ (Fig. 4.1.18) with the hepta-coordinated systems. Fig. 4.1.18 shows several absorptions in the far infrared region mainly originating from $(S_2CNR_2)^-$ vibrations. Though the geometry, coordination number and oxidation state of this complex differ with the hepta-coordinated complexes yet a tentative comparison can be made. Once $\nu_s \{W\begin{smallmatrix} S \\ | \\ S \end{smallmatrix}\}$ and $\nu_{as} \{W\begin{smallmatrix} S \\ | \\ S \end{smallmatrix}\}$ are roughly located,

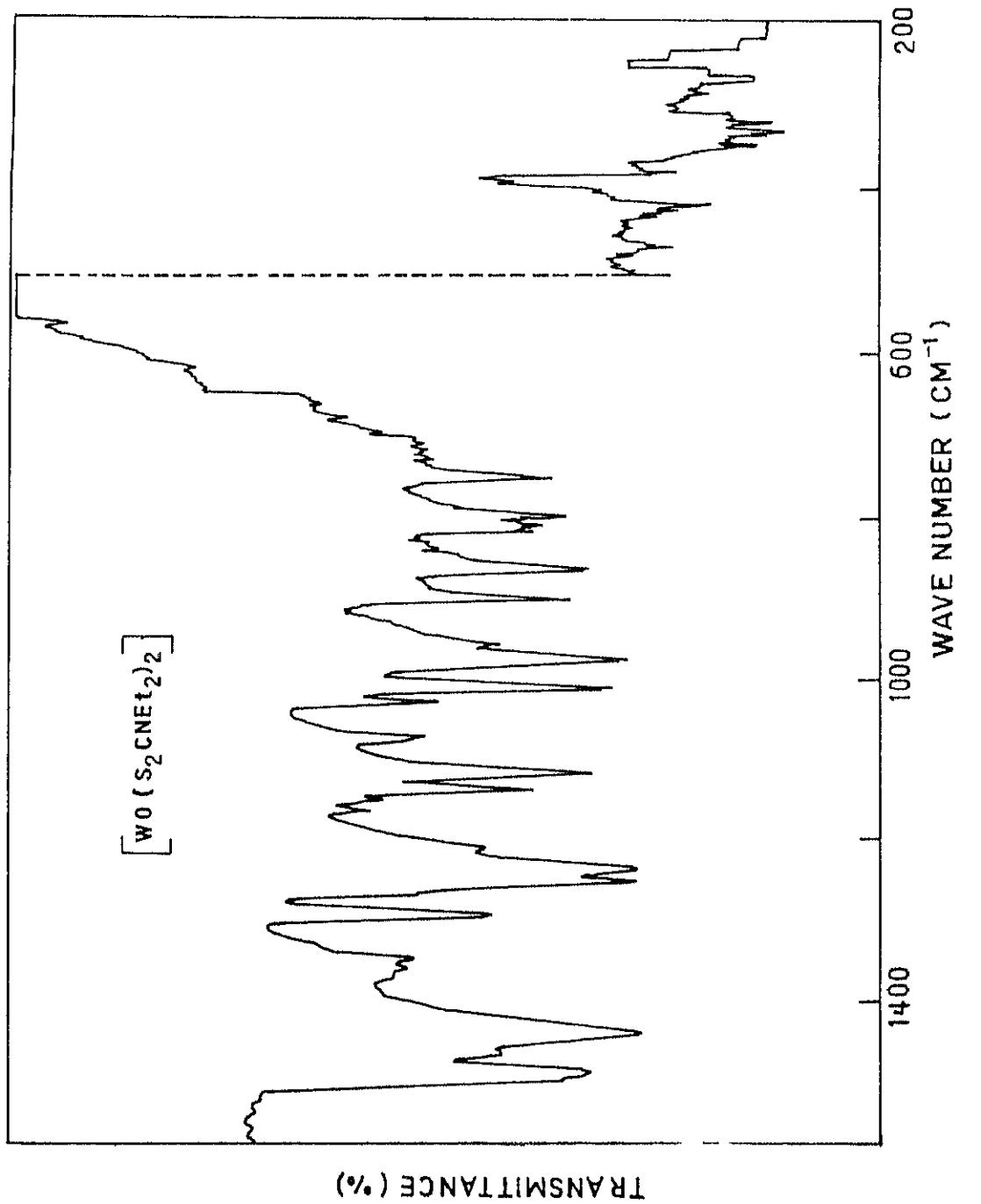


FIG. 4.1.18 INFRARED SPECTRUM

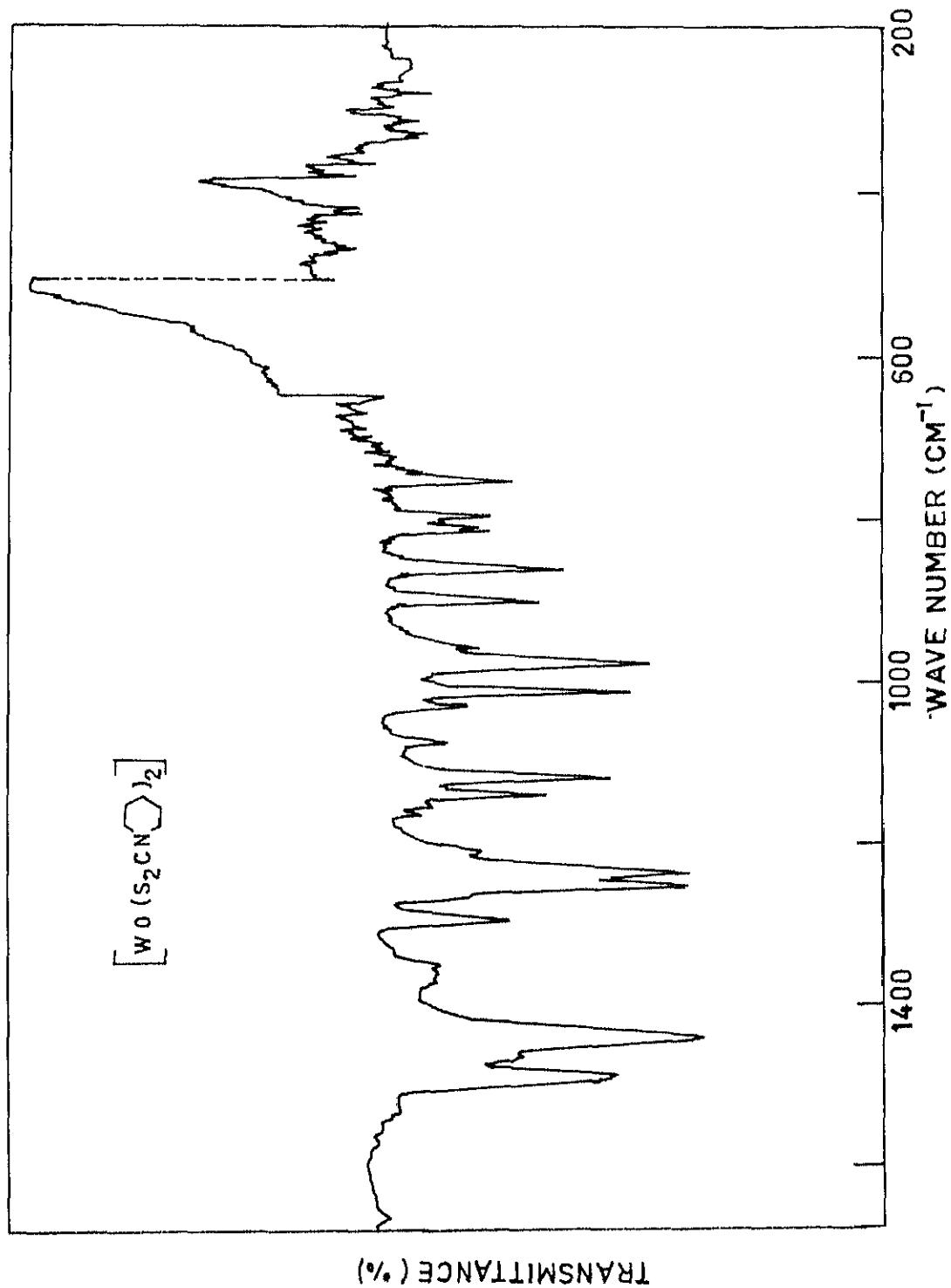


FIG 4.119 INFRARED SPECTRUM

a comparison with another class of compound, $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$ which does not have dithiocarbamate ligand, can be made. Proceeding in this direction, we identified these vibrations appearing around 370 and 350 cm^{-1} for $\nu_s \{ \text{W} \begin{array}{c} \text{S} \\ | \\ \text{S} \end{array} \}$ and $\nu_{as} \{ \text{W} \begin{array}{c} \text{S} \\ | \\ \text{S} \end{array} \}$, respectively.

In the dimeric or trimeric compounds, additional vibrations due to $\nu(\text{W-S}_b)$ should appear along with the other functionalities present. The molybdenum-sulfur-molybdenum bridging vibrations are well documented by isotopic studies.⁸⁶ For the dimeric dithiocarbamate complexes of molybdenum(V) these vibrations are reported in the literature.⁹⁷ Comparing the tungsten(V) dithiocarbamato compounds, synthesized in the present investigation, with the corresponding molybdenum analogs the $\nu(\text{W-S}_b)$ vibrations can be reasonably assigned. Thus, comparing the spectra of these tungsten complexes with the reported molybdenum analogs, assignment for these vibrations are made which are presented in Tables 4.1, 4.2 and 4.4.

An important point worth mentioning regarding $\nu(\text{W=O})$ vibrations of the tungsten compounds, is that it appears at a higher wave number compared to $\nu(\text{Mo=O})$ vibration of the corresponding molybdenum compound. Though tungsten is heavier than molybdenum yet the appearance of this vibration at higher wave number is suggestive of greater multiple bonding between tungsten and oxygen compared to molybdenum and oxygen. For the molybdenum complex $(\text{Et}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu-\text{S}_2)_2(\text{S}_2)_2]$ recent M.O. calculations suggest that the bond order of {Mo-O} moiety in the compound as high as 3.²⁹

Table 4.1. Infrared Spectral Data

Complex	ν (Mo=O) (cm ⁻¹)	ν (S-S) (cm ⁻¹)	ν (M-S _b) (cm ⁻¹)	Other important frequency (cm ⁻¹)	Reference
(Me ₄ N) ₂ [Mo ₂ O ₂ (μ -S) ₂ (S ₂) ₂]	925(s)	516(m)	467(m)	357(w), 321(w) (ν Mo-S ₂)	72
(Me ₄ N) ₂ [W ₂ O ₂ (μ -S) ₂ (S ₂) ₂]	950(s) 940(sh)	520(m)	450(m)	335(w) (ν W-S ₂)	This work
(Et ₄ N) ₂ [W ₂ O ₂ (μ -S) ₂ (S ₂) ₂]	960(s) 950(sh)	520	450(m)	335(w) (ν W-S ₂)	This work
(Et ₄ N) ₂ [W ₂ O ₂ (μ -S) ₂ (S ₂ C ₂ (COPh) ₂) ₂]	960(s) 955(sh)	-	440(m)	1660(s) (ν C=O), 1453 (ν C=C)	This work
(Et ₄ N) ₂ [W ₂ O ₂ (μ -S) ₂ (S ₂ C ₂ (COOMe) ₂) ₂]	950(s) 935(sh)	-	450(m)	1680(s) (ν C=O), 1425(s) (ν C=C)	This work
(Et ₄ N) ₂ [Mo ₂ O ₂ (μ -S) ₂ (S ₂ C ₂ (COOMe) ₂) ₂]	947(s)	-	473(m)	-	68
(Et ₄ N) ₂ [W(S ₂ C ₂ (COPh) ₂) ₃]	-	-	-	1665(s) (ν C=O), 1445(s) (ν C=C)	This work
(Et ₄ N) ₂ [Mo(S ₂ C ₂ (COPh) ₂) ₃]	-	-	-	1662(s) (ν C=O), 1450(s) (ν C=C)	133
K ₄ [W ₂ O ₂ (μ -S) ₂ (CN) ₆]	920(s)	-	470	2160(s), 2080(w) (ν C≡N)	This work

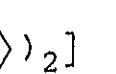
M = Mo, W; S = strong; m = medium; w = weak; S_b = bridging sulfur.

Table 4.2. Infrared Spectral Data

Complex	ν (W=O) (cm ⁻¹)	ν (W _{cent} -S _t) (cm ⁻¹)	Other W-S vibrations (cm ⁻¹)
(Et ₄ N) ₂ [WO(WS ₄) ₂]	970(s)	—	490(m), 460(m), 435(w)
(PhCH ₂ Et ₃ N) ₂ [WO(WS ₄) ₂]	960(s)	—	500(m), 470(w), 450(w)
(2 Cl-CH ₂ Me ₂ NH) ₂ [WO(WS ₄) ₂]	955(s)	—	490(m), 470(w), 430(w)
(Et ₄ N) ₂ [WS(WS ₄) ₂]	—	530(m)	500(s), 490(m), 475(w), 440(w)
(Ph ₄ As) ₂ [WS(WS ₄) ₂]	—	525(m)	500(s), 490(m), 470(w)

s = strong; m = medium; w = weak.

Table 4.3. Infrared Spectral Data

Complex	ν (M=O) (cm ⁻¹)	ν (M-S _t) (cm ⁻¹)	ν (S-S) (cm ⁻¹)	References
[MoO(S ₂)(S ₂ CNPr ₂)]	917(s)	-	555(m)	141
Cs ₂ [MoO(S ₂) ₂ (O ₂ CCOS)]		-	530(m)	144, 145
[WO(S ₂)(S ₂ CNET ₂) ₂]	940(s)	-	552(m)	Present work
[WO(S ₂)(S ₂ CNPr ₂) ₂]	945(s)	-	554(m)	Present work
[WO(S ₂)(S ₂ CN ) ₂]	940(s)	-	552(m)	Present work
[WS(S ₂)(S ₂ CNET ₂) ₂]	-	500(m)	545(m)	Present work
[WS(S ₂)(S ₂ CNPr ₂) ₂]	-	500(m)	550(m)	Present work
[WS(S ₂)(S ₂ CN ) ₂]	-	500(m)	540(m)	Present work
(Et ₂ NH ₂)[WO(S ₂) ₂ (S ₂ CNET ₂)]	880(s)	-	540(m)	Present work
(Pr ₂ NH ₂)[WO(S ₂) ₂ (S ₂ CNPr ₂)]	880(s)	-	535(m)	Present work
[WO(S ₂ CNET ₂) ₂]	980(s)	-	-	Present work
[WO(S ₂ CN ) ₂]	980(s)	-	-	Present work

M = Mo, W; s = strong, w = weak, m = medium, S_t = terminal sulfur.

Table 4.4. Infrared Spectra Data

Complex	ν (M=S) (cm ⁻¹)	ν (M-S _t) (cm ⁻¹)	ν (M-S _b) (cm ⁻¹)	Reference
[Mo ₂ O ₂ (μ -S) ₂ (S ₂ CNEt ₂) ₂]	967, 952	—	477, 340	97
[Mo ₂ OS(μ -S)(S ₂ CNEt ₂) ₂]	962, 956	544	471, 337	97
[Mo ₂ S ₂ (μ -S)(S ₂ CNEt ₂) ₂]	—	548(m), 538(sh)	463, 334	97
[W ₂ O ₂ (μ -S) ₂ (S ₂ CNEt ₂) ₂]	985(s), 970(sh)	—	470(m), 338(w)	Present work
[W ₂ O ₂ (μ -S) ₂ (S ₂ CN(cyclohexyl)) ₂]	985(s), 975(sh)	—	465(m), 335(w)	Present work
[W ₂ OS(μ -S) ₂ (S ₂ CNEt ₂) ₂]	980(s)	540(m)	465(m), 335(w)	Present work
[W ₂ OS(μ -S) ₂ (S ₂ CN(cyclohexyl))]	980(s)	538(m)	460(m), 330(w)	Present work
[W ₂ S ₂ (μ -S) ₂ (S ₂ CNEt ₂) ₂]	—	535(m), 535(sh)	460(m), 332(w)	Present work

M = Mo, W; s = strong; m = medium; w = weak; S_t = terminal sulfur; S_b = bridging sulfur.

Trinuclear clusters $[\text{WO}(\text{WS}_4)_2]^{2-}$ and $[\text{WS}(\text{WS}_4)_2]^{2-}$ show $\nu(\text{W-O}_t)$ and $\nu(\text{W-S}_t)$ of the central tungsten in the regions 955-970 cm^{-1} and 525-530 cm^{-1} , respectively. There are several other absorptions in the region 430-500 cm^{-1} arising from $\nu(\text{W-S}_t)$ and $\nu(\text{W-S}_b)$. Infrared spectra of this series of compounds are reproduced in Figs. 4.1.3 to 4.1.5 and data are tabulated in Table 4.2.

Other Ligand Vibrations

Dithiolene ligand vibrations

Cycloaddition of alkynes to the M-S-X unit is well documented in the literature.^{76,77} Such reactions are not known with tungsten compounds. Here two activated acetylenes DBA (dibenzoyl-acetylene) and DMA (dimethylacetylene dicarboxylate) have been used to study this type of reaction with the tungsten-sulfur system. The detailed study on analogous molybdenum systems is well documented.⁸⁰ Amongst these, the most important is the insertion of DMA into Mo-S bond of the compound $(\text{Et}_4\text{N})_2^-$ $[\text{Mo}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{78}$, forming vinyl disulfide ligated compound. However, under refluxing conditions the vinyl disulfide compound rearranges to dithiolene isomer.⁷⁹ Reaction of $(\text{Et}_4\text{N})_2[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]$ with activated acetylenes has been carried out. Infrared spectra of these complexes are reproduced in Figs. 4.1.6 and 4.1.7. To distinguish the mode of insertion of the activated acetylenes across W-S or S-S bond of coordinated

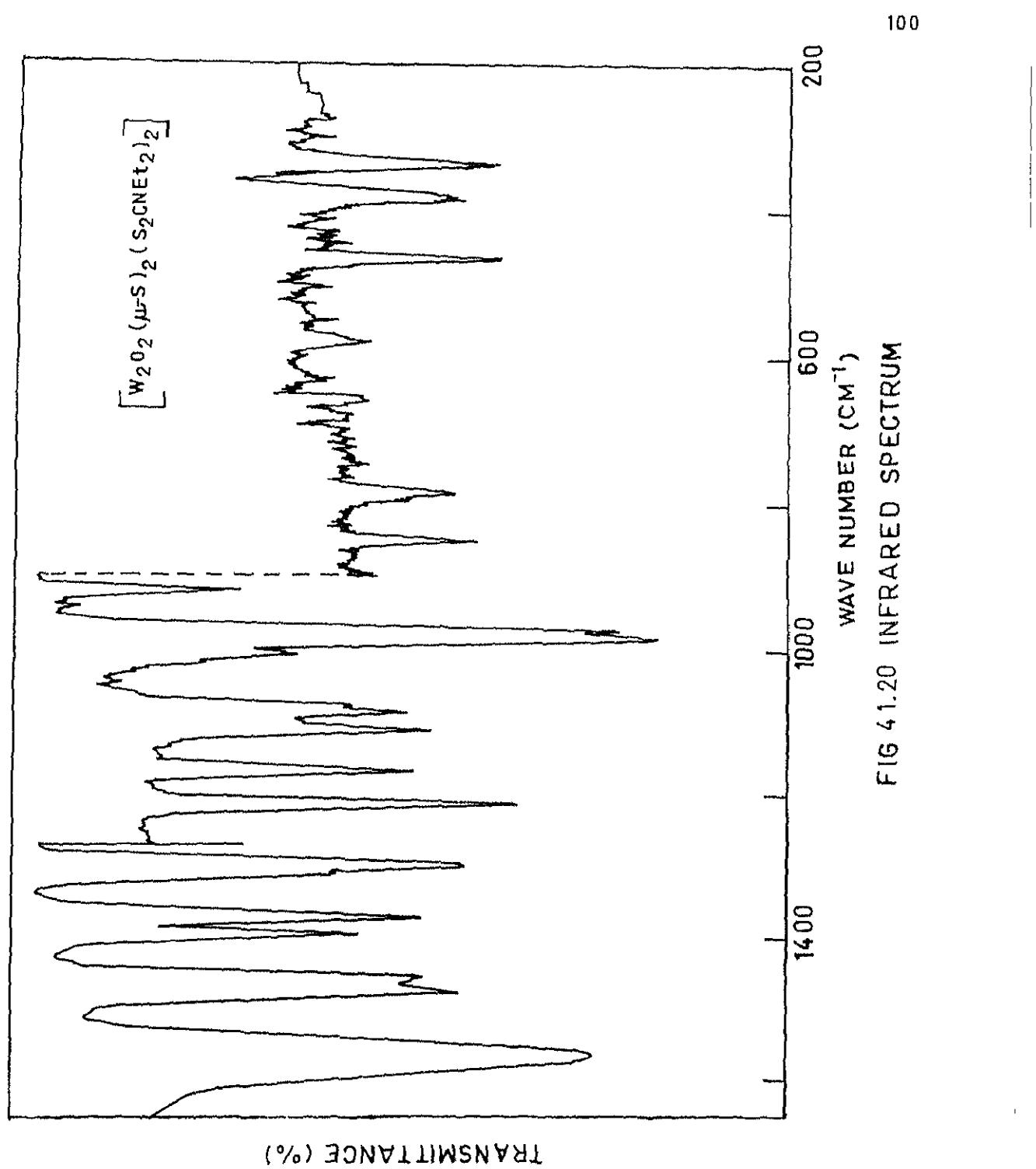


FIG 41.20 INFRARED SPECTRUM

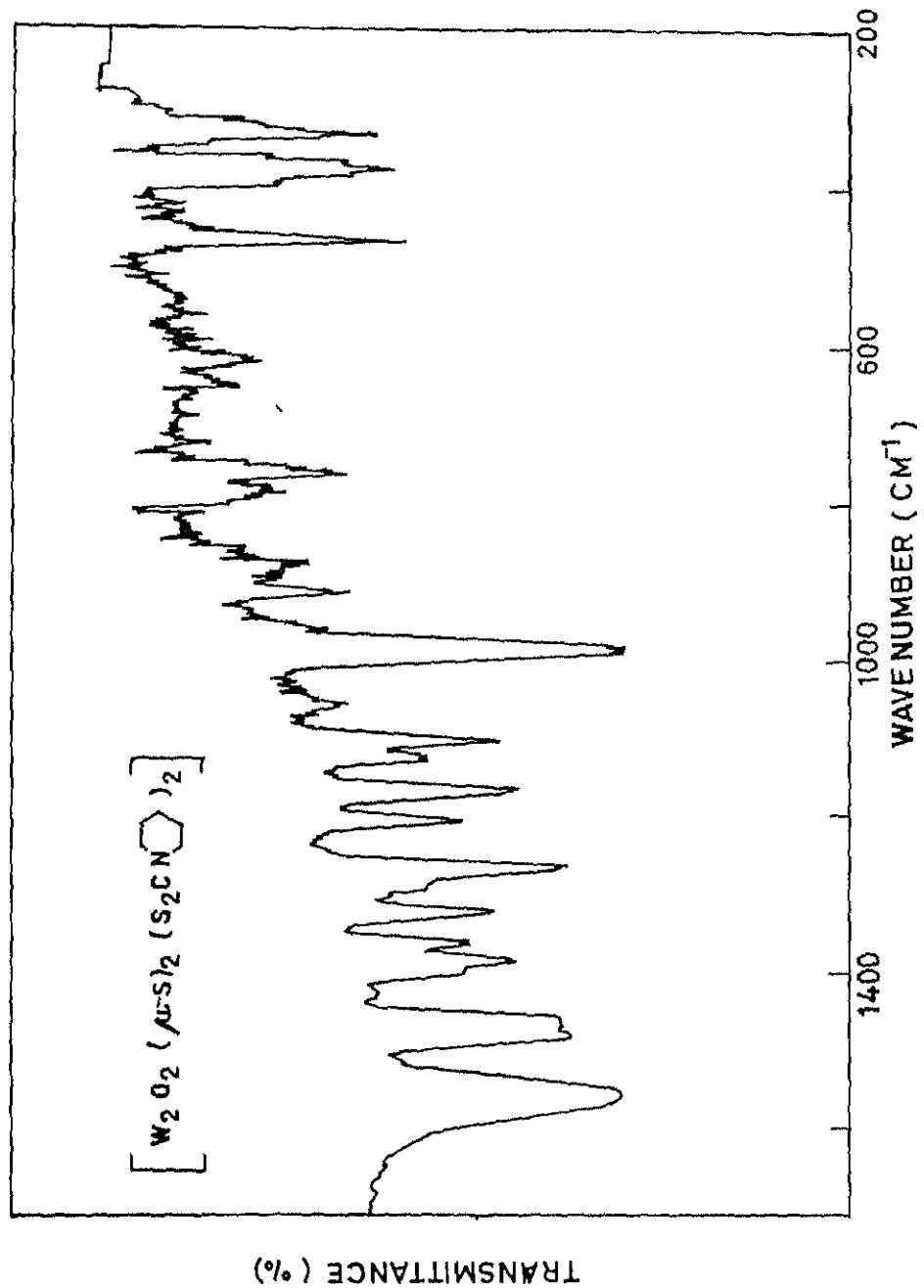


FIG. 4121 INFRARED SPECTRUM

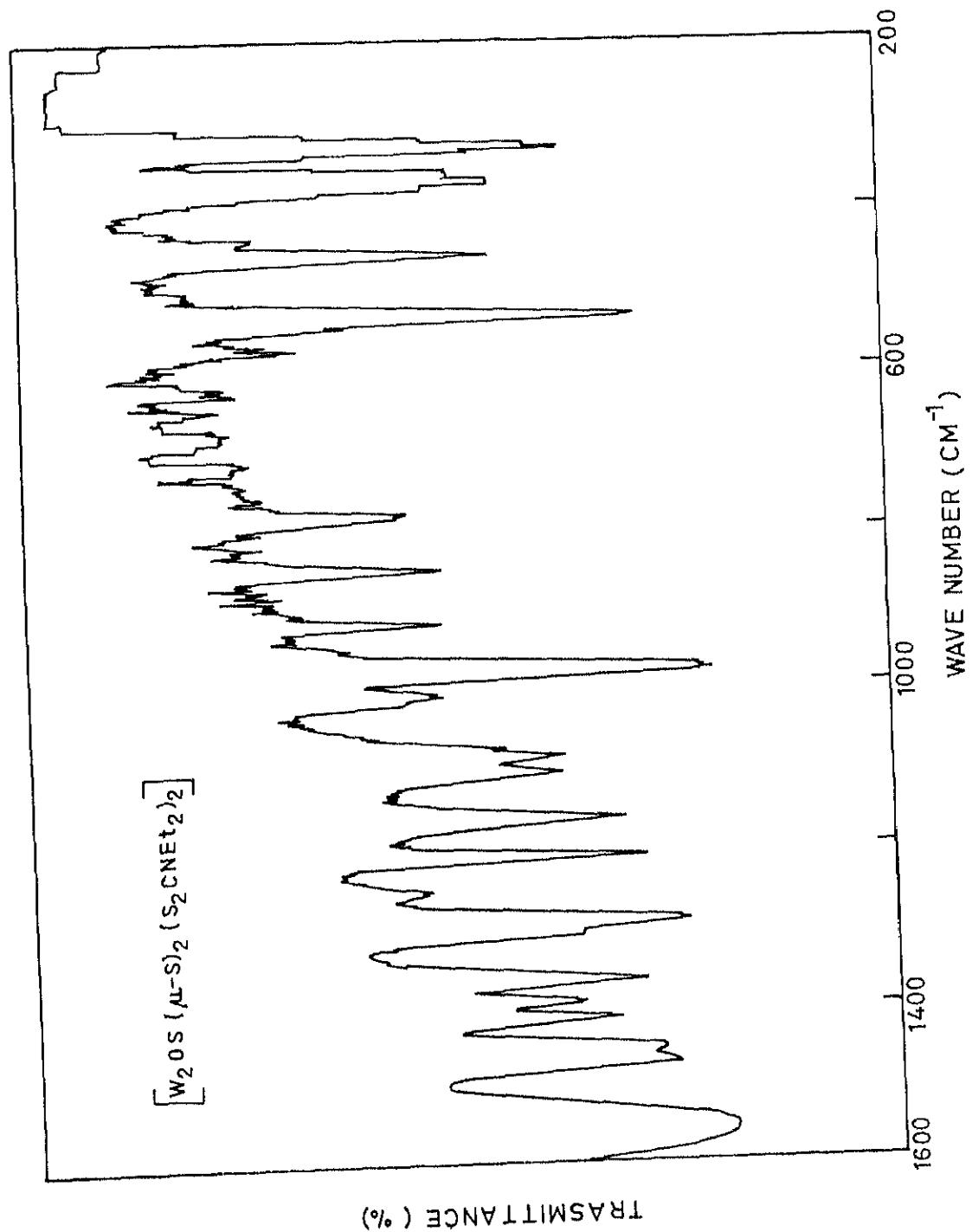


FIG. 4.1.22 INFRARED SPECTRUM

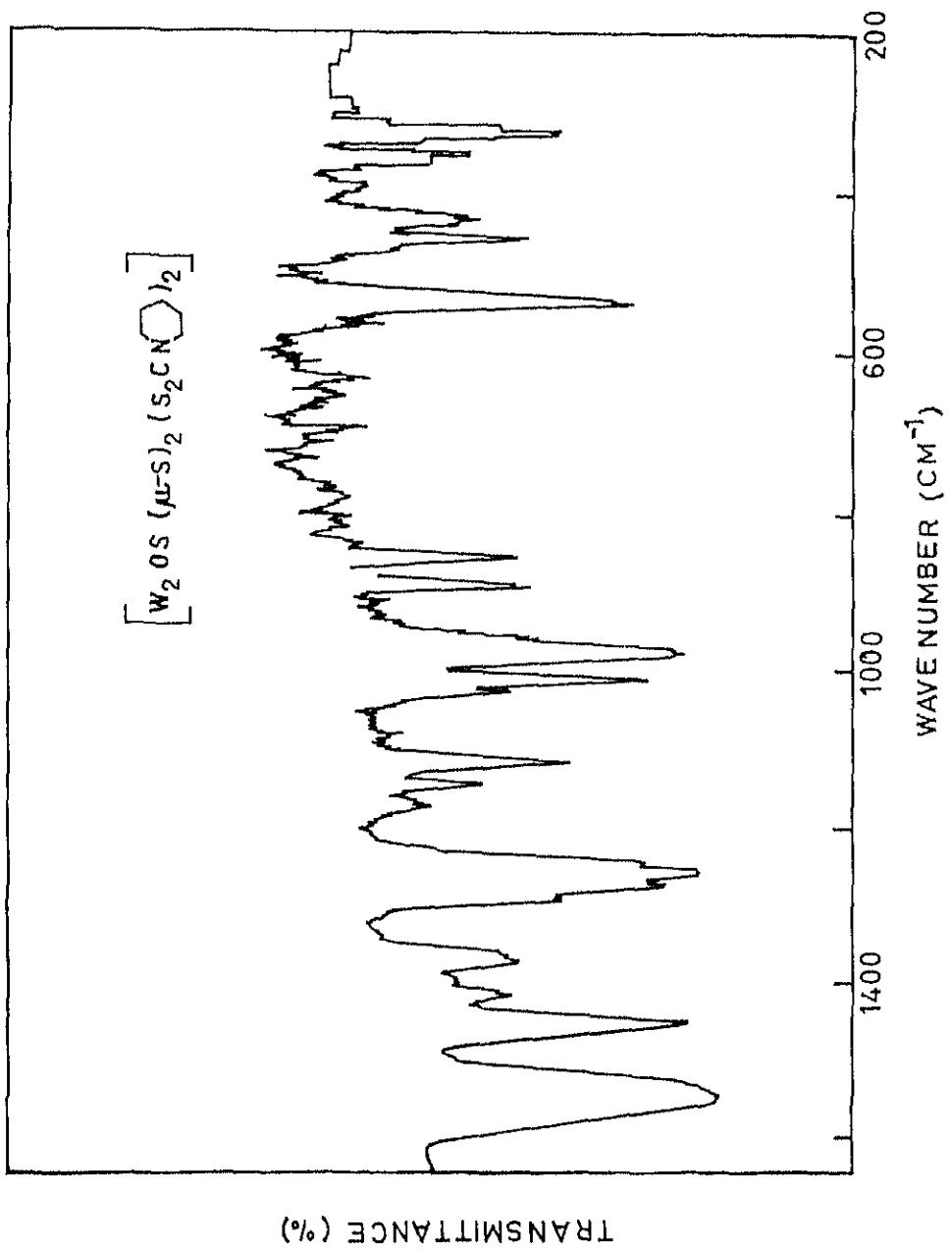


FIG. 4. INFRARED SPECTRUM

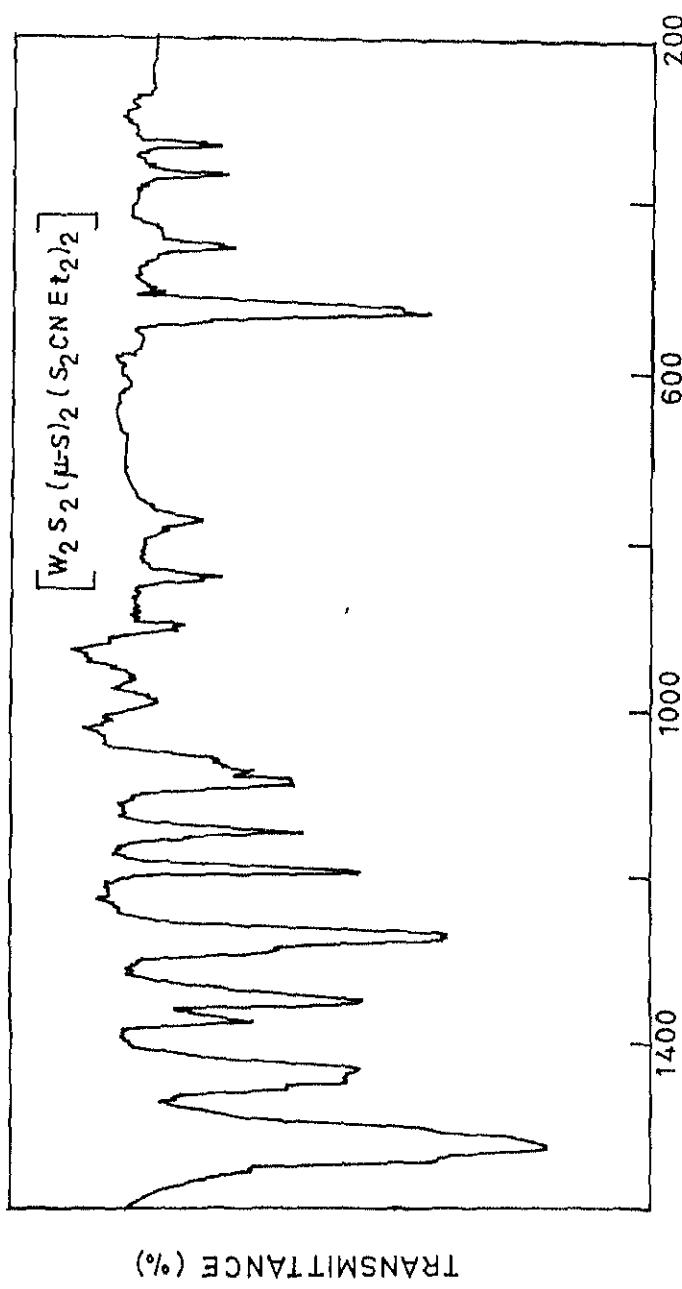


FIG. 4.1.24 INFRARED SPECTRUM

S_2^{2-} ligand, IR spectra may be helpful if one can assign the presence of W-C bond in the vinyl disulfide complex. In the spectra of such complexes there are several vibrations in the low frequency region and the task of identifying such vibrations is not possible. For the dithiolene complexes C=C stretching frequency could be a rough measure of C=C bond strength. This stretching frequency is mainly dependent on the nature of the substituent group on the carbon atoms. Thus, to distinguish vinyl disulfide or dithiolene mode of coordination of the insertion reaction, ν (C=C) could help in understanding the mode of reaction. The infrared spectral data presented in Table 4.1 for the complexes reported here suggest that ν (C=C) appears in the range where the substituent groups on carbon are sulfur along with functional group (-COPh or -COOMe) and there is no dramatic change in this frequency when compared to other dithiolene complexes. Thus, we can tentatively assign the formation of dithiolene ligand formation instead of vinyl disulfide formation which has been established by ^{13}C NMR studies (vide infra). The assignment of ν (W-S) vibration arising from dithiolene coordination is going to be difficult as they are often strongly coupled with π -ring vibrations of the ligand.¹⁴³ Thus a serious discussion in this regard is not possible.

The spectra of other dithiolene complexes of tungsten reported here are presented in Figs. 4.1.6 to 4.1.8 and important assignments are made by comparing the spectra of the corresponding molybdenum analogs (Table 4.1).

Infrared spectra of cyanosubstituted complex $K_4[W_2O_2(\mu-S)_2^-(CN)_6] \cdot 3H_2O$ shows $\nu(CN)$ at $2075(s)$ and $2070(w) \text{ cm}^{-1}$ (Fig. 4.1.9) which is slightly more than the free cyanide.¹⁴⁶ It is difficult to assign $\nu(W-C)$ in this complex, as there are some other vibrations arising from $\nu(W-S_b)$. However, a tentative assignment can be made by comparing it with other similar complexes where no metal-carbon bond is involved. Proceeding in this direction, vibration at 450 cm^{-1} may be attributed to $\nu(W-S_b)$ and rest of the vibrations at 420 , 335 and 310 cm^{-1} can reasonably be assigned to $\nu(W-C)$.

Many of the complexes synthesized here, have dialkyl dithiocarbamate ligand attached to the metal. Spectra of similar complexes have been studied extensively. Mode of coordination of this ligand can be understood by monitoring the splitting of $\nu(C-S)$ near 1000 cm^{-1} and the appearance of $\nu(CN)$ in the region $1450-1600 \text{ cm}^{-1}$.¹⁴⁷ Infrared stretching frequencies for such complexes which appear above 1500 cm^{-1} suggest that dithiocarbamate acts as a bidentate ligand. The $\nu(W-S_{dtc})$ appears in the region $400-300 \text{ cm}^{-1}$ which is mixed with some other vibrations, some times. Thus, the correct assignment of $\nu(W-S_{dtc})$ is not straightforward except in the case of $[WO(S_2CNR_2)_2]$ where it appears at 355 , 340 and 320 cm^{-1} ($R = Et$).

4.2.2 Electronic Spectra

The electronic absorption spectra of $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ ion and other persulfido complexes are reproduced in Figs. 4.2.3,

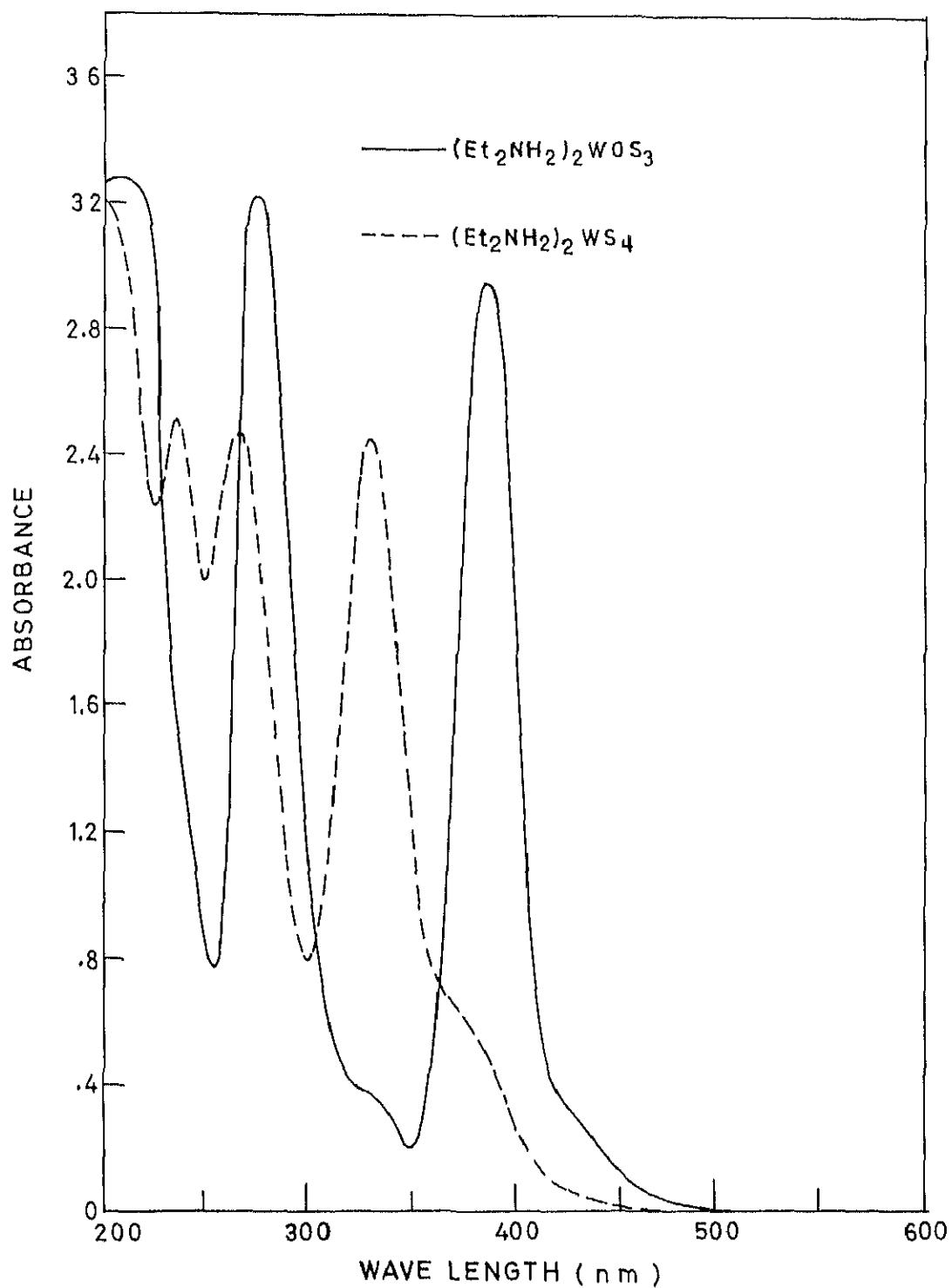


FIG 4.2.1 ELECTRONIC SPECTRA

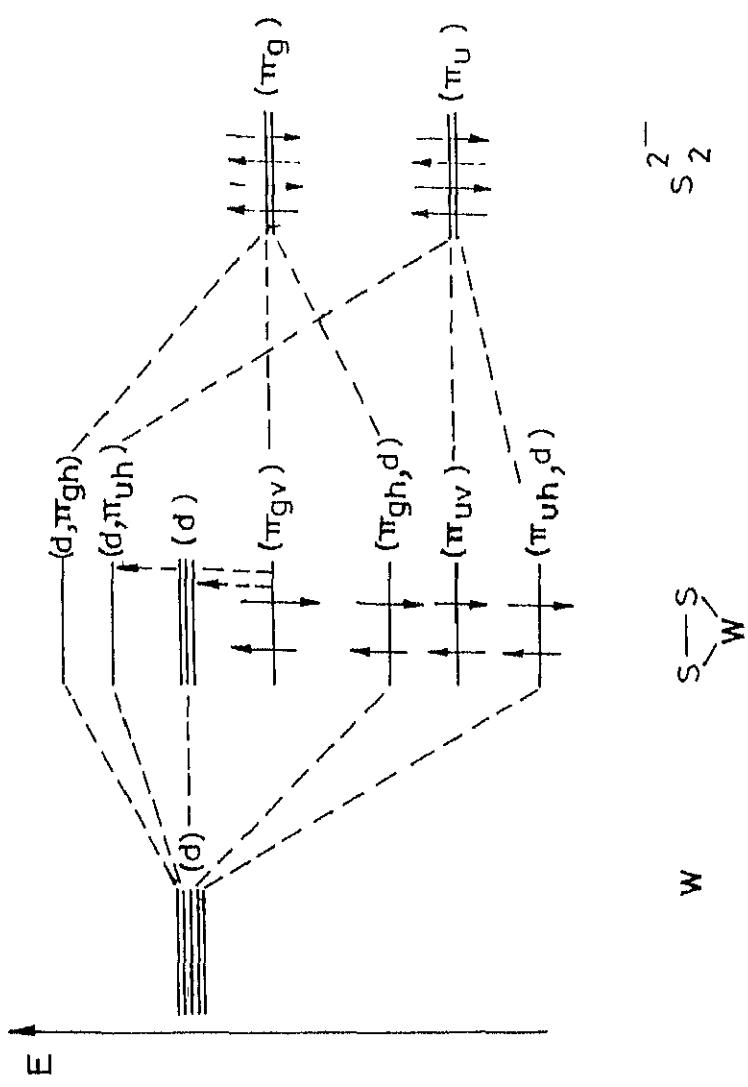


FIG 4.2.2 QUALITATIVE MO SCHEME FOR PERSULFIDO COMPLEXES

4.2.9 to 4.2.11. The electronic absorption maxima and the corresponding extinction coefficients for these complexes are tabulated in Table 4.5 and 4.6. When S_2^{2-} is bonded in side on (η)² fashion to a metal, the π^* orbital of S_2^{2-} splits into strongly interacting π_h^* orbital in the $\{M\overset{S}{\diagdown}\overset{S}{\diagup}\}$ plane and a weakly interacting π_v^* orbital perpendicular to the $\{M\overset{S}{\diagdown}\overset{S}{\diagup}\}$ plane. The longest wavelength band in $[MoO(S_2)(S_2CNET_2)_2]$ occurs around 580 n.m. and is assigned to a LMCT (ligand to metal charge transfer) of the type $\pi_v^*(S) \rightarrow d(Mo)$.¹⁵⁰ This assignment has been taken valid for the complex ion, $[Mo_2O_2(\mu-S)_2(S_2)_2]^{2-}$ where molybdenum is still in the high oxidation state.⁸⁶ The position of these bands is affected by several factors for example, the oxidation state of the metal, the presence of other ligands and the involvement of metal-metal bond in dimeric complexes. These factors determine the energy of LUMO and its metal character. A qualitative MO scheme for $\{M\overset{S}{\diagdown}\overset{S}{\diagup}\}$ moiety (side on coordination bond symmetry C_{2v}) is shown in Fig. 4.2.2. This MO scheme is similar to the one developed for dioxygen metal complexes.^{150,151}

For the complex ion, $[Mo_2O_2(\mu-S)_2(S_2)_2]^{2-}$ the assignments of absorption bands are according to the discussion mentioned above. Thus, the lowest energy band around 460 n.m. is assigned to $\pi_v^*(S) \rightarrow d(Mo)$ (LMCT) and a relatively weak band around 377 n.m. has been assigned to $\sigma \rightarrow \sigma^*$ charge transfer arising from Mo-Mo bonding. This is consistent with Mo-Mo bond distance and the diamagnetic nature of the compound.⁸⁶ The high energy

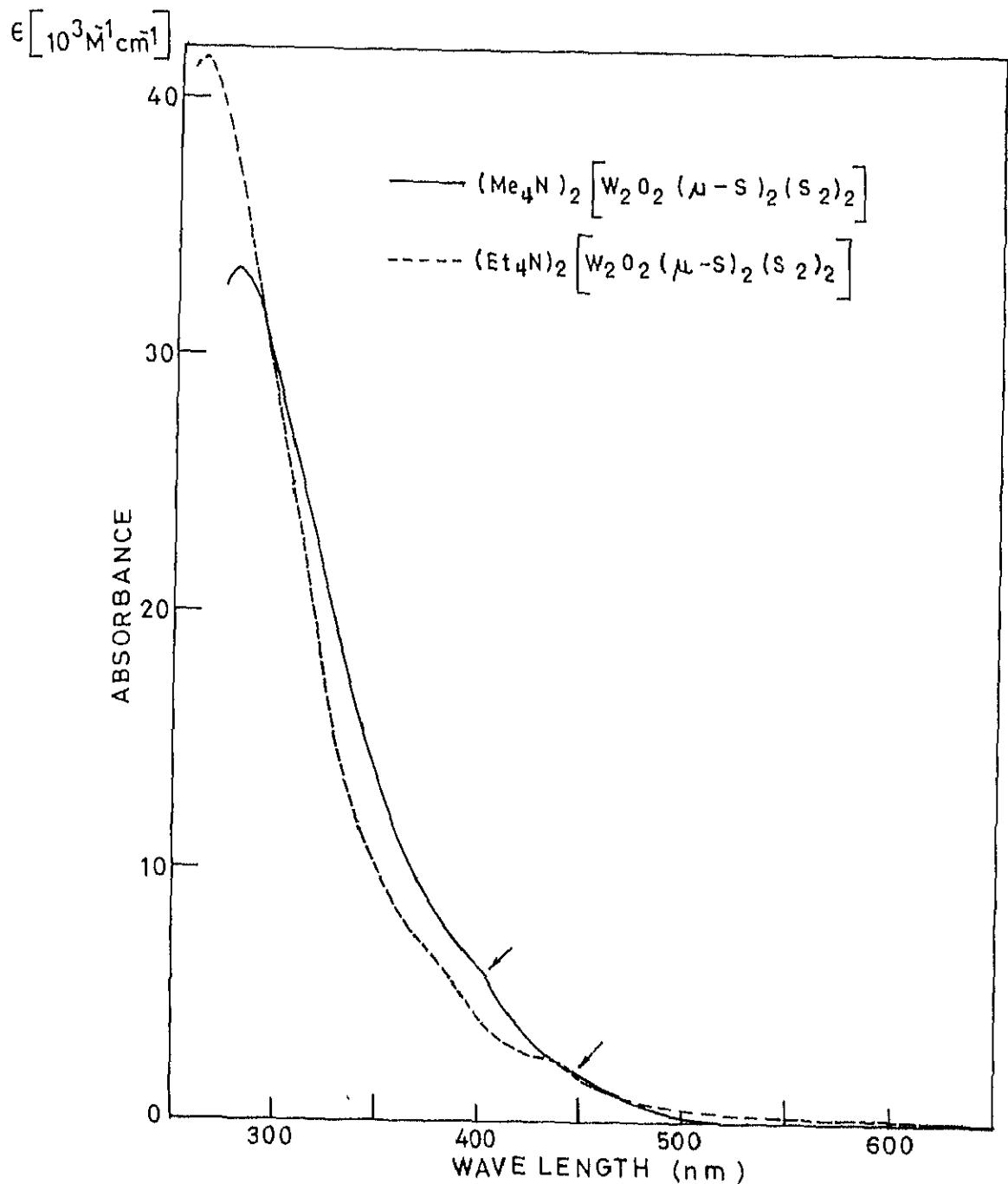


FIG 4.2.3 ELECTRONIC SPECTRA

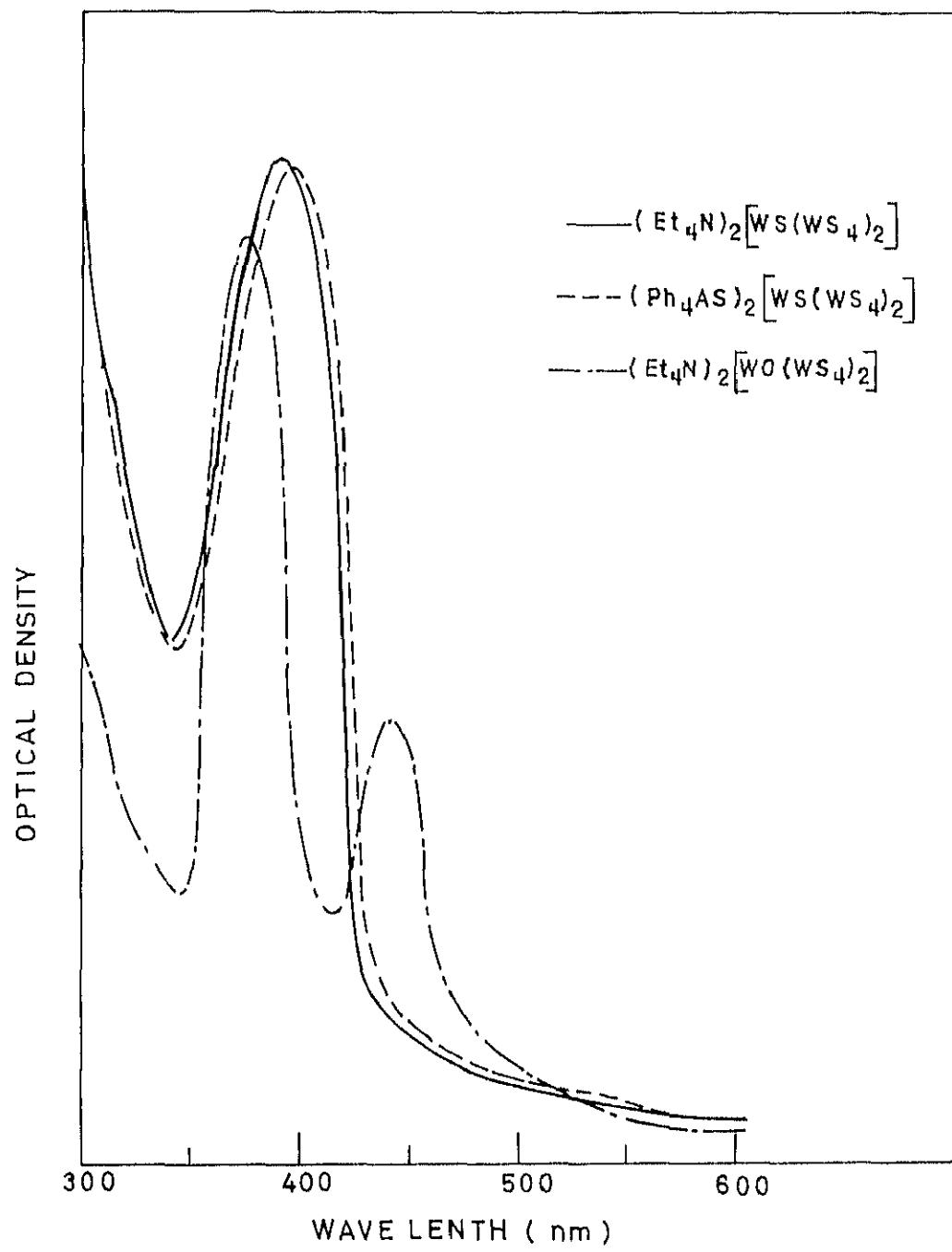


FIG 4.2.4 ELECTRONIC SPECTRA

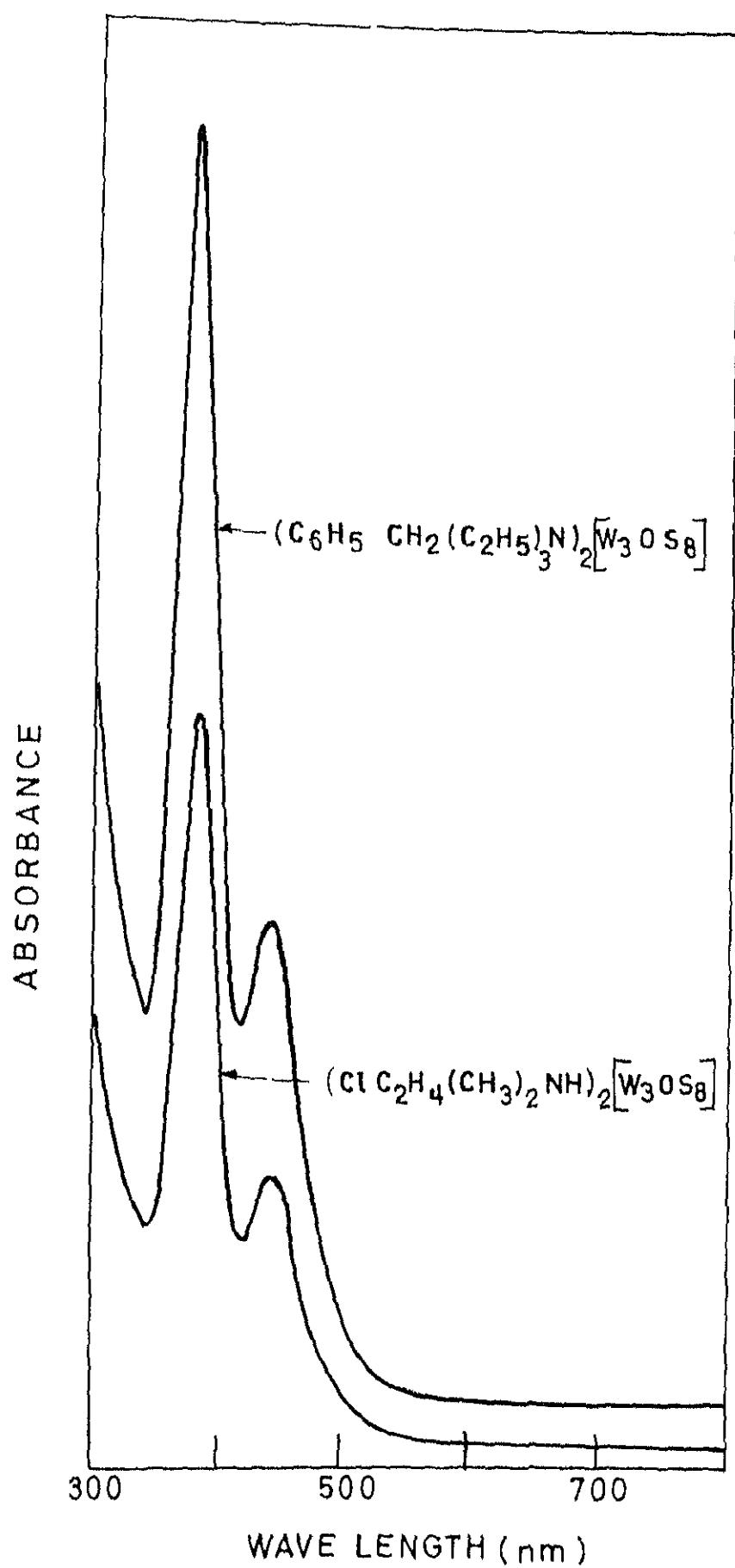


FIG. 4.2.5 ELECTRONIC SPECTRA

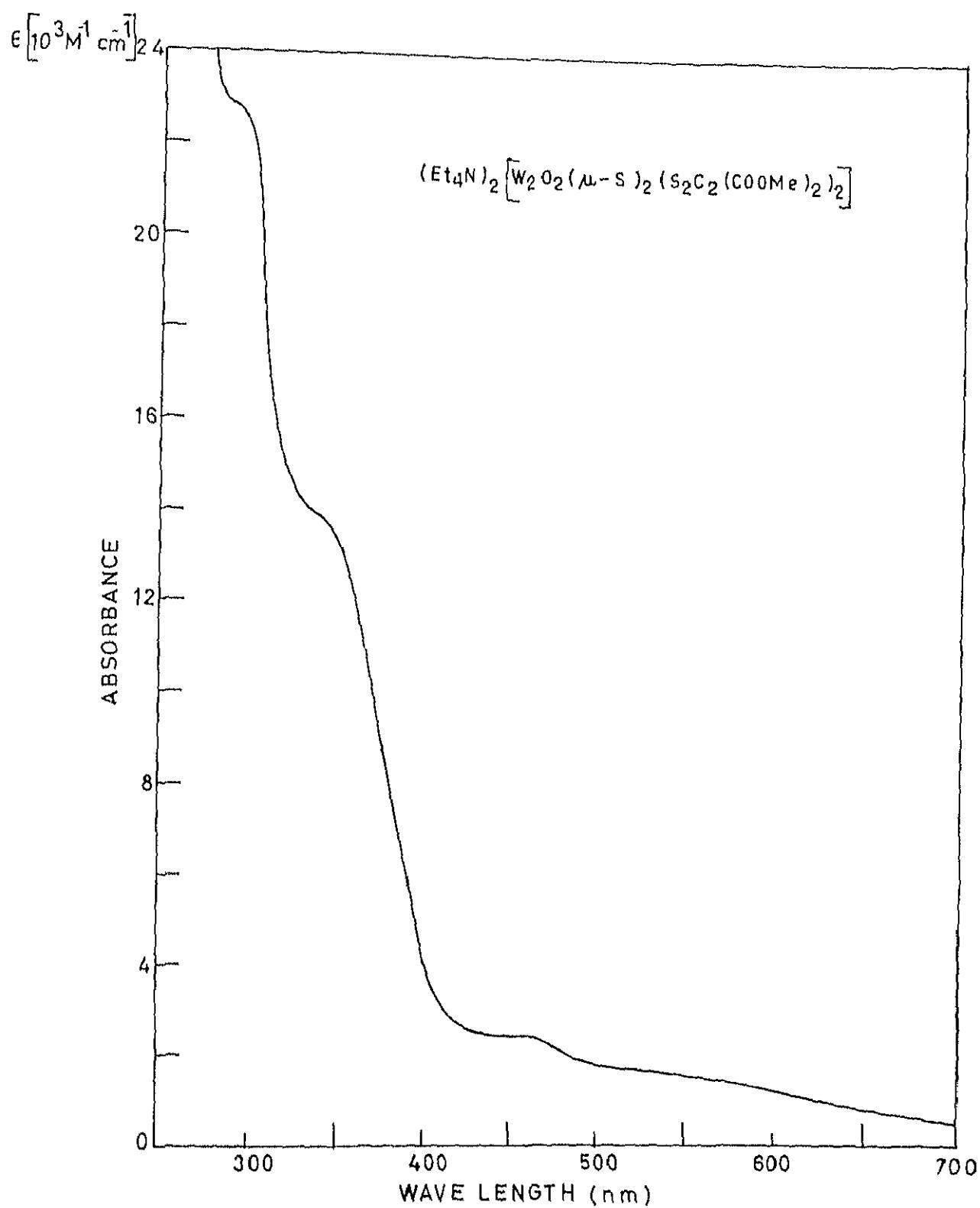


FIG 4.2.6 ELECTRONIC SPECTRUM

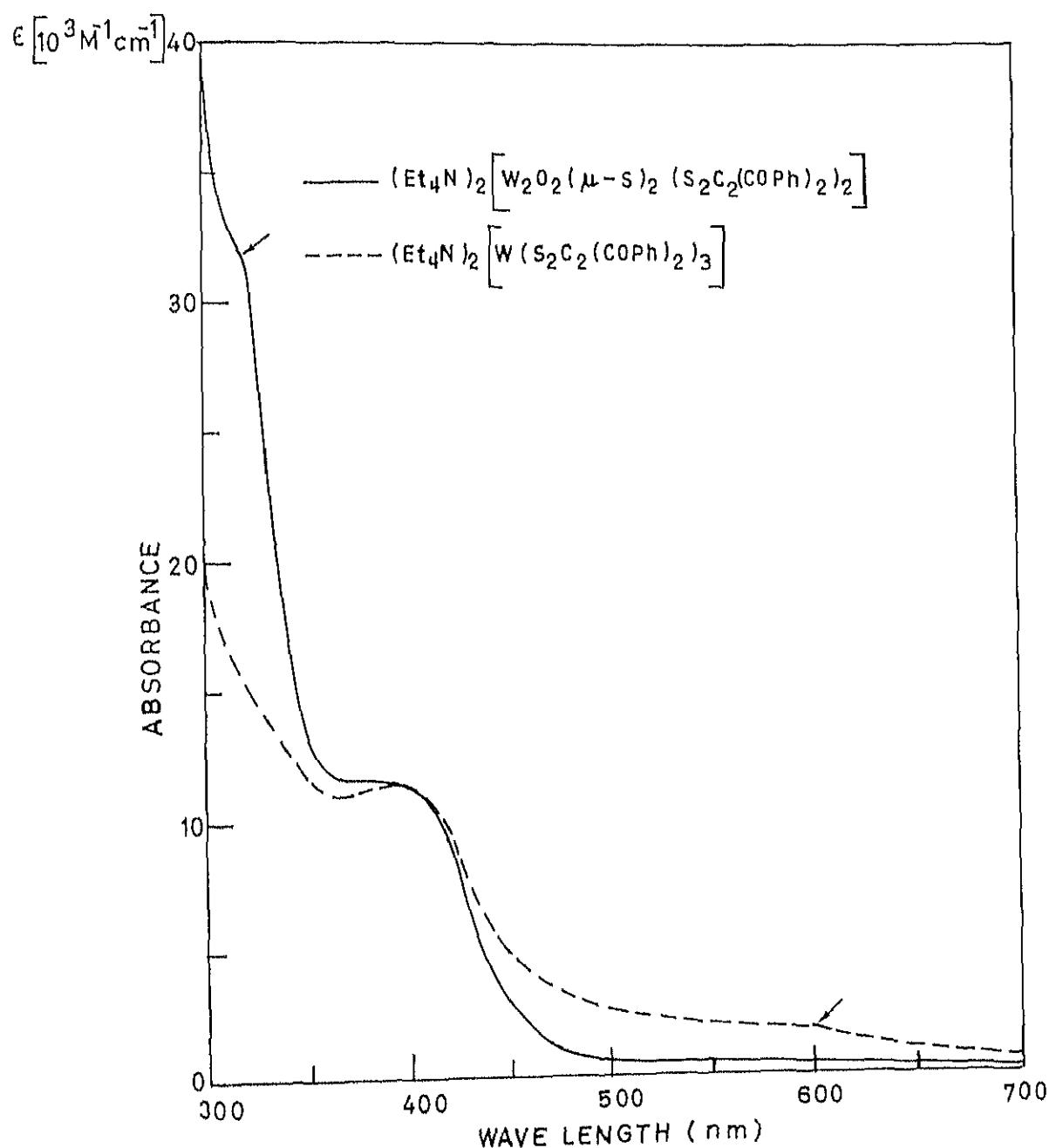


FIG 4.2.7 ELECTRONIC SPECTRA

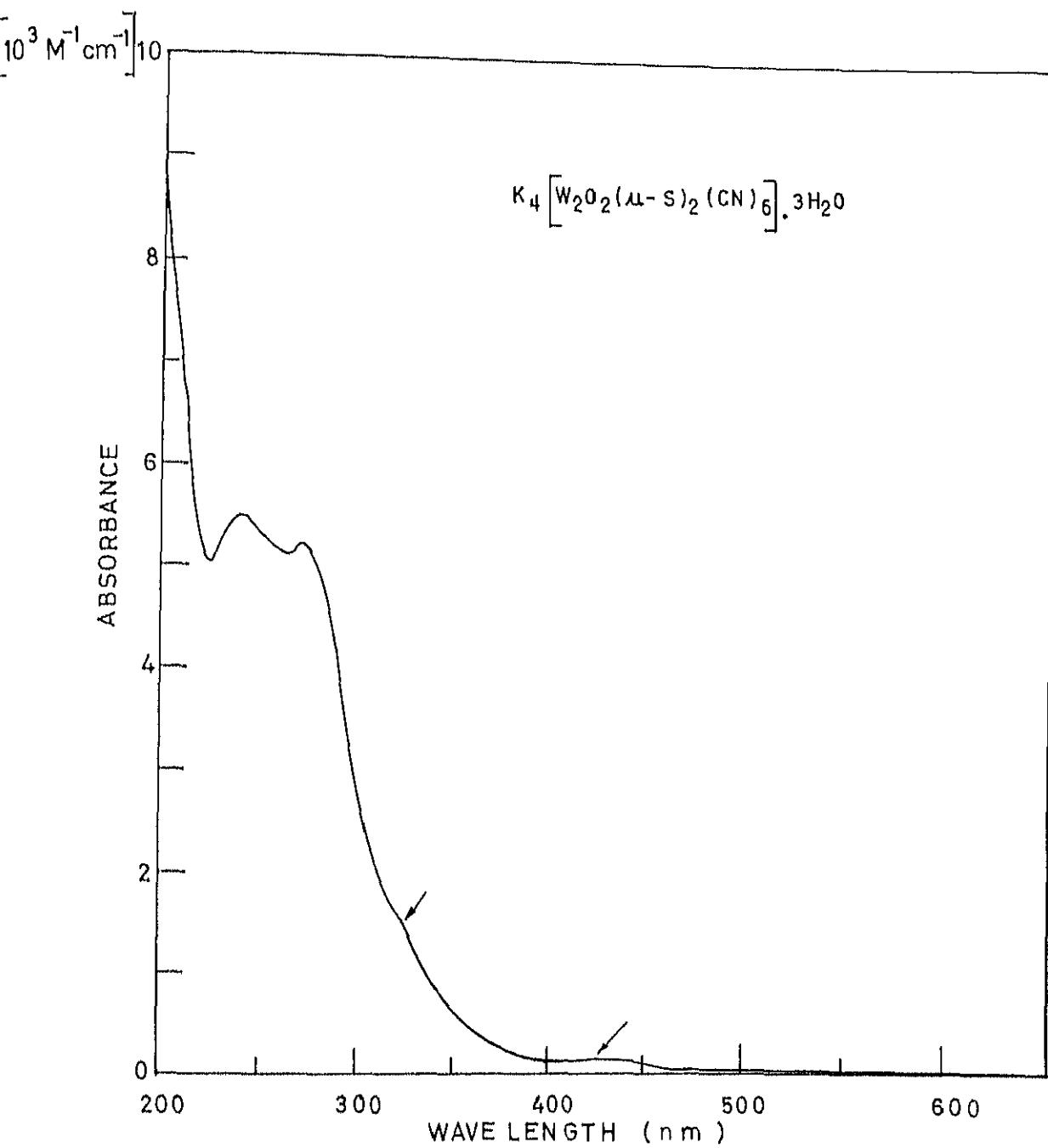


FIG 4.28 ELECTRONIC SPECTRUM

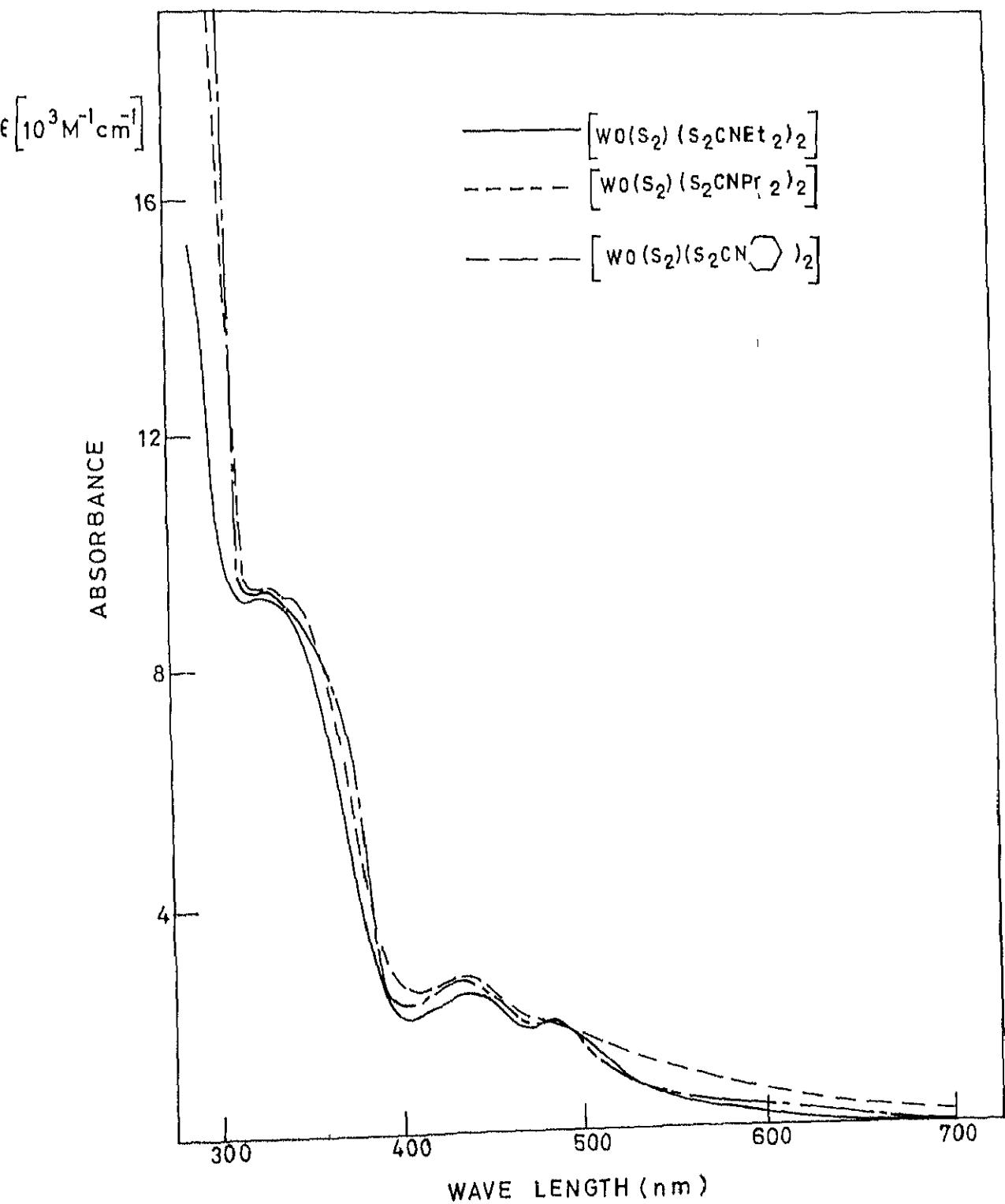


FIG 4.2.9 ELECTRONIC SPECTRA

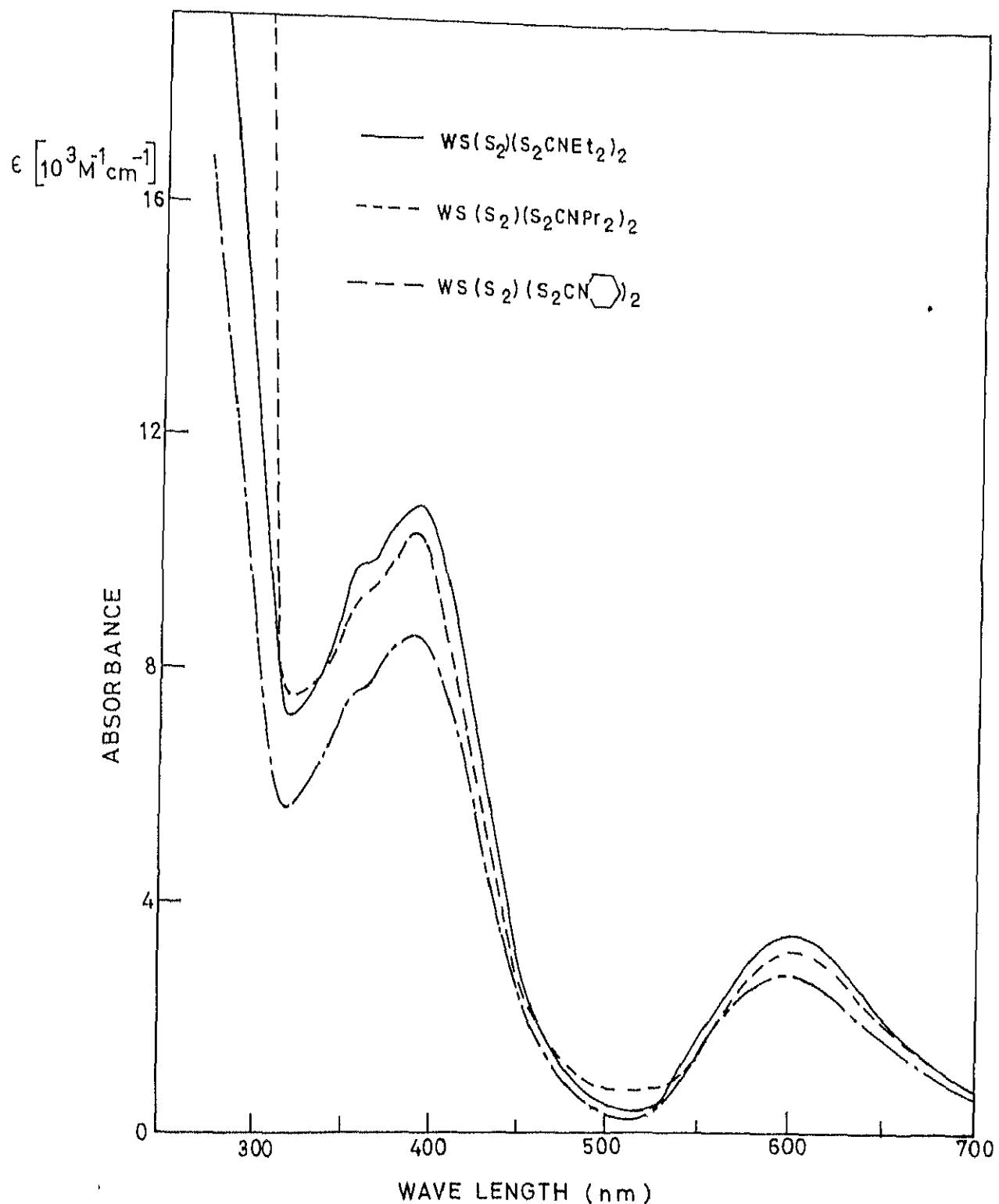


FIG. 4 2 10 ELECTRONIC SPECTRA

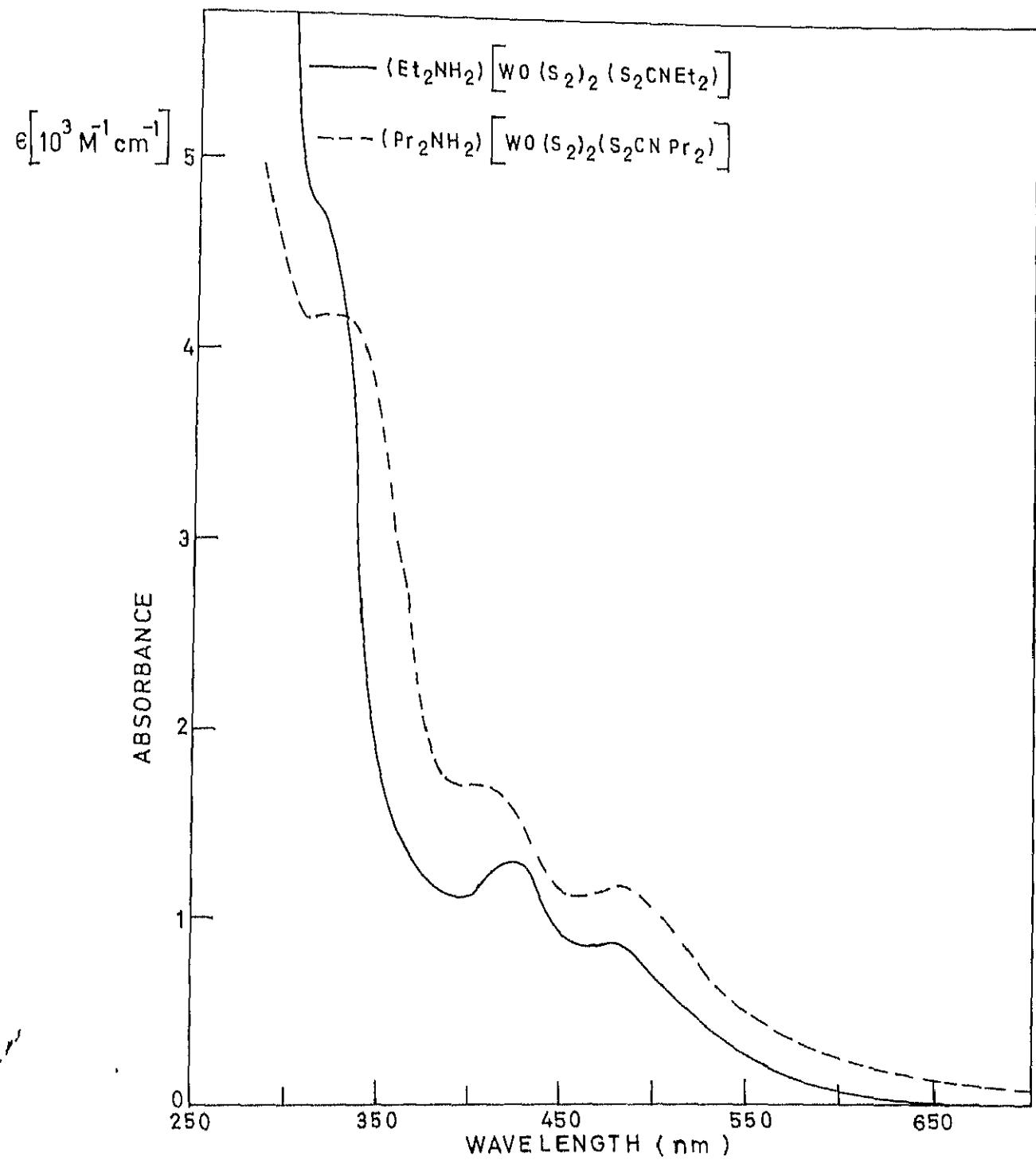


FIG 4.2.11 ELECTRONIC SPECTRA

bands in u.v. region are assigned to charge transfer originating from sulfido group to metal center and $\pi \rightarrow \pi^*$ transition of $\{Mo\begin{smallmatrix} S \\ | \\ S \end{smallmatrix}\}$ moiety.⁸⁶

For the complex ion, $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ a similar argument can be put forward to assign the electronic transitions because this complex is isostructural to its molybdenum analog (X-ray powder pattern vide 4.5.7) and shows similar diamagnetic behaviour. Thus, the red colour of $(Et_4N)_2[W_2O_2(\mu-S)_2(S_2)_2]$ is due to the transition of the type $\pi_v^*(S) \rightarrow d(W)$ which appears around 430 n.m. The second band around 380 n.m. which appears as shoulder, is relatively weak in nature and may be due to $\sigma \rightarrow \sigma^*$ transition originating from W-W bonding. The high energy u.v. band at 260 n.m. is then due to charge transfer from bridging sulfur to tungsten and/or $\pi \rightarrow \pi^*$ transition in $\{W\begin{smallmatrix} S \\ | \\ S \end{smallmatrix}\}$ moiety. Salts of the ion $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ are not stable enough to carry out Resonance Raman study. Hence any confirmation of these electronic transitions could not be done.

In case of the complexes of the type $[WO(S_2)(S_2CNET_2)_2]$, the arguments given above for $\{W\begin{smallmatrix} S \\ | \\ S \end{smallmatrix}\}$ moiety should be valid, considering the presence of the coligand, dithiocarbamate. The electronic spectrum of free dithiocarbamate exhibits three bands in the u.v. region and on complexation, the shift in these bands are not significant.^{139, 140} The nature of these transitions is intraligand: $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$. Keeping this in mind, the high energy bands in the u.v. region could be assigned to dithiocarbamate intraligand transitions.

Comparing the corresponding molybdenum complex, the longest wavelength band at 480 n.m. for $[\text{WO}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2]$ is assigned to $\pi_v^*(\text{S}) \rightarrow d(\text{W})$ transition. The second band around 435 n.m. could be due to $\pi_{\text{gv}} \rightarrow \pi_{\text{uh}}$ charge transfer of the $\text{W} \begin{array}{c} \text{S} \\ | \\ \text{S} \end{array}$ moiety. Both of these transitions are ligand to metal charge transfer type. The extinction coefficient values of these two transitions support this assignment because the first transition takes place into an empty metal d-orbital and the second to the antibonding MO which is predominantly metal in character. If the transitions originate from (π_{gh}, d) and $\pi_{\text{uh}}, d)$ orbitals to the antibonding orbitals (d, π_{uh}) and (d, π_{gh}) , the extinction coefficient should be high.¹⁵⁰

For the compounds of the type $[\text{WS}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2]$ the highest energy band around 360 n.m. is due to intraligand charge transfer transition of dithiocarbamate ligand. The lowest energy band is then assigned to $\pi_v^*(\text{S}) \rightarrow d(\text{W})$ transition. However, the middle band at 390 n.m. has a very high extinction coefficient. The corresponding oxo analog shows a band at 435 n.m. with low extinction coefficient. The position of this band at 390 n.m. compared to 435 n.m. for the oxo analog and its intense nature suggests that the origin of this transition may be of the type $(\pi_{\text{gh}}, d)/(\pi_{\text{uh}}, d) \rightarrow (d, \pi_{\text{uh}})/d, \pi_{\text{gh}})$.

The electronic absorption spectrum of $(\text{R}_2\text{NH}_2)[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNR}_2)]$ is similar to that of $[\text{WO}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2]$. By following the arguments stated above, the bands around 475, 415 and 310 n.m.

can be assigned to $\pi_v^*(s) \rightarrow d(W)$, $\pi_{gv} \rightarrow \pi_{uh}$ and intraligand charge transfer transitions, respectively.

Electronic absorption spectra of dinuclear dithiocarbamato tungsten(V) complexes are reproduced in Figs. 4.2.13 and 4.2.14. Lozano and coworkers have isolated similar complexes with different bulky substituents on dithiocarbamate, following a multistep 139,140 process. They could observe very weak d-d transitions because of the appreciable solubility of their complexes. The diethyl and piperidine dithiocarbamates used here, give similar tungsten complexes, which have unfortunately restricted solubility. Thus, the expected d-d transition could not be selected. The spectra of this series of complexes are predominantly charge transfer type. A comparison of the electronic spectrum of free dialkyl dithiocarbamate with the electronic spectra of these complexes suggests that the high energy u.v. bands are originating from the coordinated dithiocarbamate ligand. There is only one absorption in the visible region ranging from 415 to 422 n.m. which may be assigned to charge transfer transition from ligand (bridged disulfide and/or dithiocarbamate ligand) to tungsten.

The electronic spectra of dithiolene ligated complexes containing $\{W_2O_2(\mu-S)_2\}^{2+}$ core, recorded in the range 700-300 n.m. exhibit only two transitions (Fig. 4.2.6 and 4.2.7). There are dramatic changes in the band position as well as their extinction coefficient values, with the change of the substituent group in $S_2C_2R_2^{2-}$ ($R = COPh, COOMe$, Table 4.5). Similar observations have

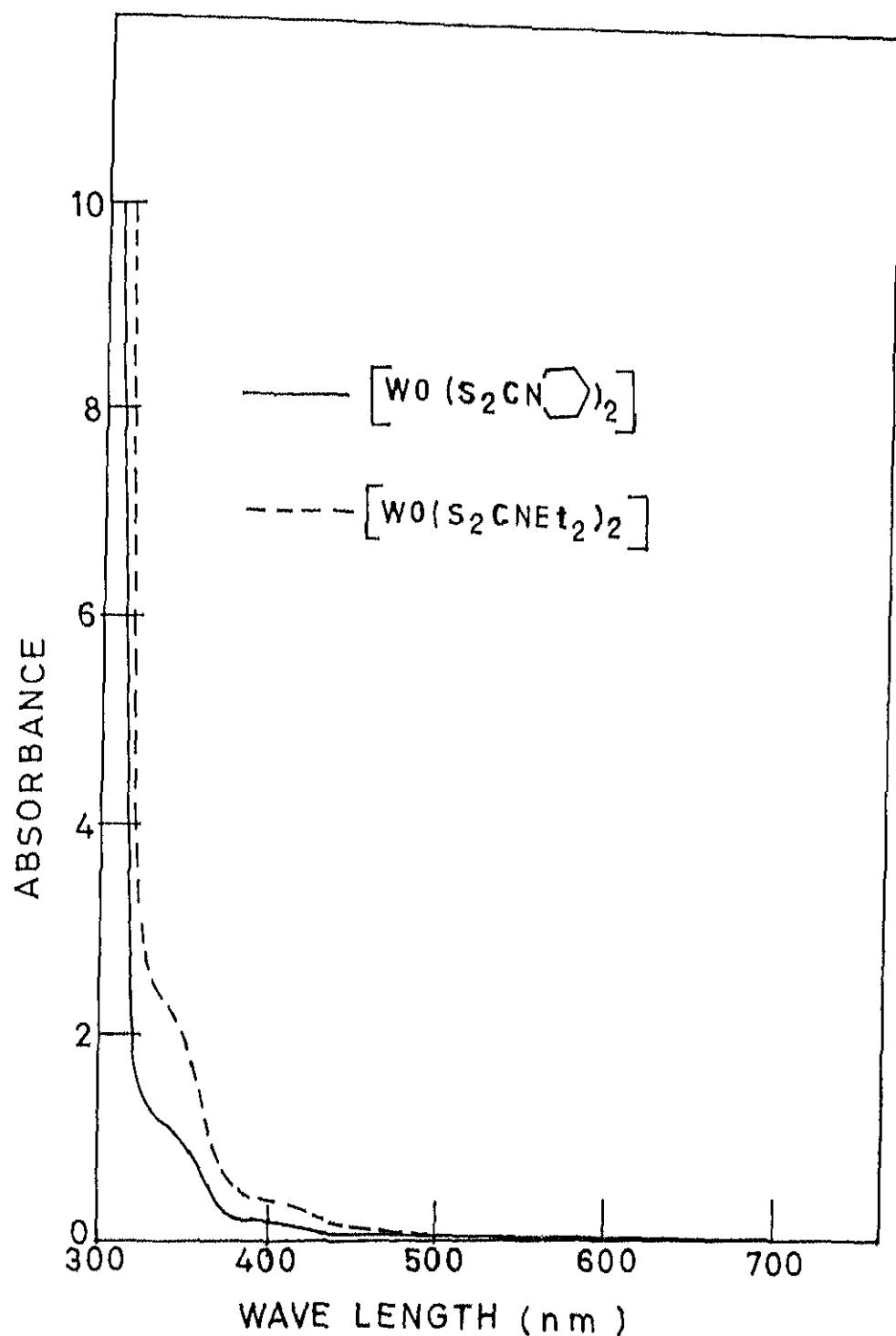


FIG. 4.2.12 ELECTRONIC SPECTRA

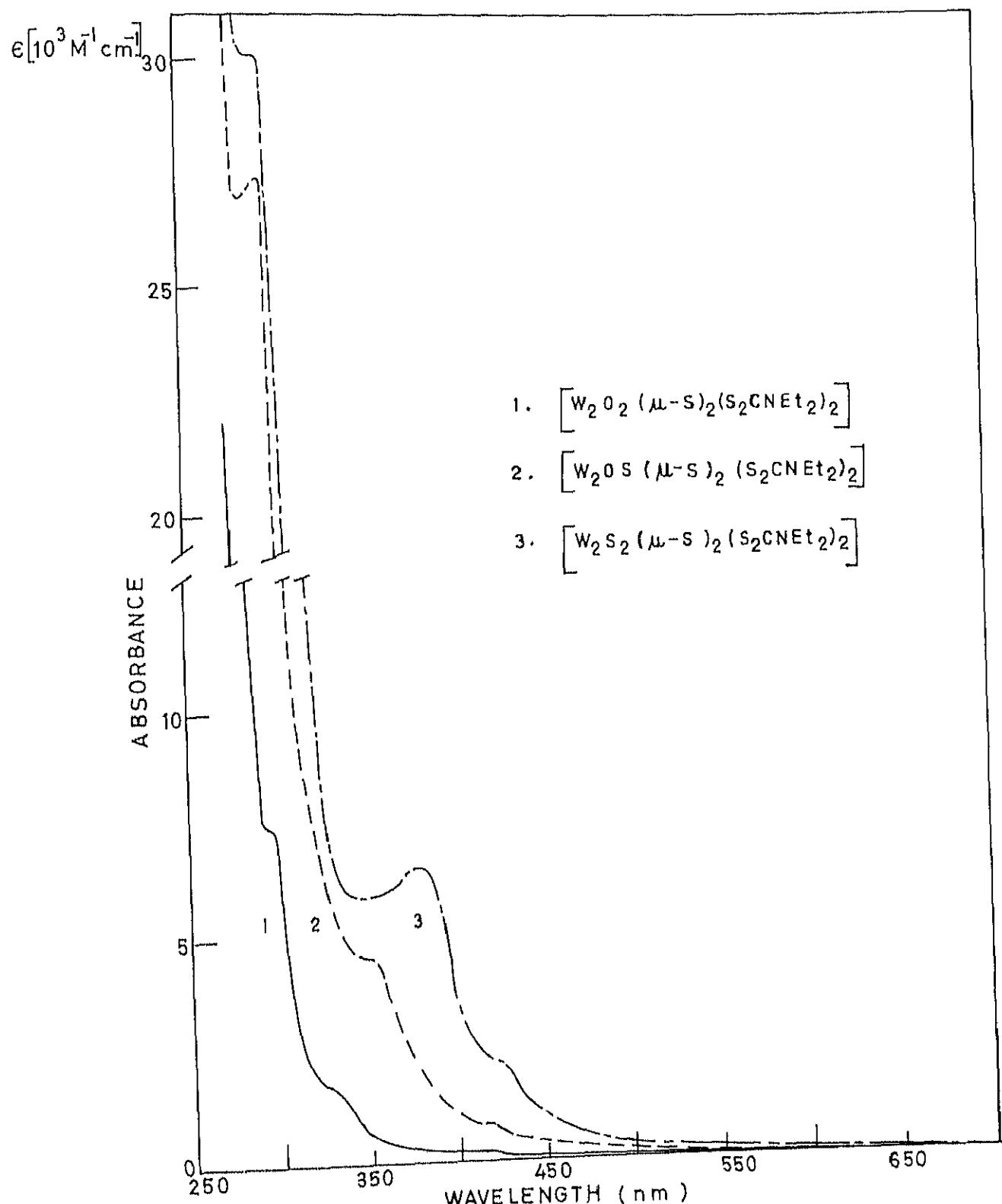


FIG. 4 2 13 ELECTRONIC SPECTRA

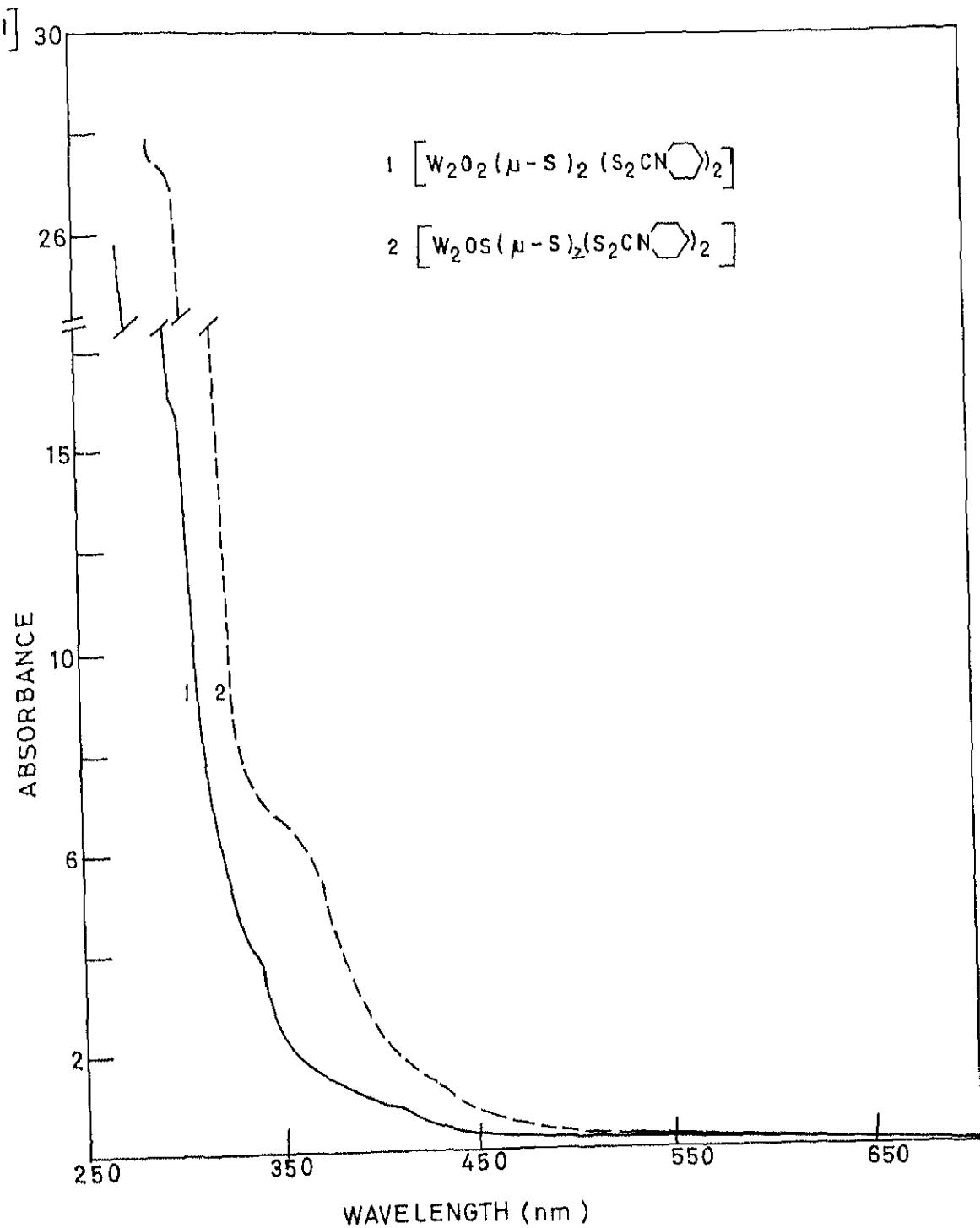


FIG 4.2.14 ELECTRONIC SPECTRA

been observed in similar dithiolene complexes.¹⁴⁸ The electronic spectrum of $(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$, reproduced in Fig. 4.2.7 shows only two absorptions in the visible region at 600 and 448 n.m. whereas the corresponding molybdenum complex $(Et_4N)_2-[Mo(S_2C_2(COPh)_2)_3]$ shows three absorptions at 592, 412 and 336 n.m. in its electronic spectrum.¹³¹ Stiefel and coworkers have also synthesized similar tris-dithiolene complexes of W(IV) and Mo(IV) with different substituents. They also experienced similar discrepancy in these systems.¹⁵²

The electronic spectrum of $K_4[W_2O_2(\mu-S)_2(CN)_6] \cdot 3H_2O$ is reproduced in Fig. 4.2.8. The electronic spectrum of this complex has many absorptions in the u.v. region at 325, 268, 238 and 210 n.m. which may be attributed to charge transfer transitions originating from coordinated cyanide.¹⁴⁶ The absorption at 425 n.m. can be assigned to charge transfer from bridged sulfido groups to tungsten(V). It is important to note that in the complex, $[W_2O_2(\mu-S)_2-(S_2CNET_2)_2]$ an absorption appears at 415 n.m. Hence the absorption in the range 415-420 n.m. in sulfido bridged complexes, studied here may be mainly originating from the bridged sulfido groups to tungsten(V) charge transfer.

Electronic absorption spectra of trinuclear clusters $[W^{IV}O(W^{VI}S_4)_2]^{2-}$ and $[W^{IV}S(W^{VI}S_4)_2]^{2-}$ are reproduced in Figs. 4.2.4 and 4.2.5 and data are presented in Table 4.6. All these transitions are of charge transfer type and have been discussed in detail by several groups.^{40,86}

Table 4.5 Electronic Spectral Data

Complex	Solvent	λ_{max} (ϵ) (nm)	Reference
$(\text{Me}_4\text{N})[\text{Mo}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]$	CH_3CN	463 (2.0×10^3) 377(sh) 305 (10.6×10^3) 278 (11.3×10^3)	86
$(\text{Et}_4\text{N})_2[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]$	CH_3CN	430 (2.3×10^3) 380(sh) 260 (41.3×10^3)	This work
$(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]$		440 (2.0×10^3) 400(sh) 280 (33.2×10^3)	This work
$\text{K}_4[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{CN})_6]$	H_2O	425 (0.15×10^3) 325 (1.4×10^3) 268 (5.1×10^3) 238 (5.5×10^3) 210 (6.3×10^3)	This work
$(\text{Et}_4\text{N})_2[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{C}_2(\text{COPh})_2)_2]$	DMF	382 (11.5×10^3) 316 (31.8×10^3)	This work
$(\text{Et}_4\text{N})_2[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$	DMF	460 (2.4×10^3) 345 (14×10^3)	This work
$(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]$	DMF	557 (6.1×10^3) 498(sh) 325 (46×10^3)	148
$(\text{Et}_4\text{N})_2[\text{W}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$	DMF	600 (1.9×10^3) 448 (11.6×10^3)	This work
$(\text{Et}_4\text{N})_2[\text{Mo}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$	DMF	592 (5.8×10^3) 412 (9.4×10^3) 336 (10.5×10^3)	133

Table 4.6 Electronic Spectral Data

Complex	Solvent	λ_{max} (nm)
$(\text{Et}_4\text{N})_2[\text{WS}(\text{WS}_4)_2]$	CH_3CN	538(sh)
		390
$(\text{Ph}_4\text{As})_2[\text{WS}(\text{WS}_4)_2]$	CH_3CN	540(sh)
		390
$(\text{Et}_4\text{N})_2[\text{WO}(\text{WS}_4)_2]$	CH_3CN	440
		378
$(\text{PhCH}_2\text{Et}_3\text{N})_2[\text{WO}(\text{WS}_4)_2]$	CH_3CN	440
		378
$(2\text{Cl-C}_2\text{H}_4\text{Me}_2\text{NH})_2[\text{WO}(\text{WS}_4)_2]$	CH_3CN	440
		380

Table 4.7 Electronic Spectral Data

Complex	Solvent	λ_{max} (nm)	(ϵ)	Reference
1	2	3	4	
$[\text{MoO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	CH_3CN	578	(1.2×10^3)	63
		391	(3.4×10^3)	
$[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	CH_2Cl_2	480	(1.8×10^3)	This work
		438	(2.4×10^3)	
		340(sh)		
		320	(9.3×10^3)	
$[\text{WO}(\text{S}_2)(\text{S}_2\text{CNPr}_2)_2]$	CH_2Cl_2	480	(1.8×10^3)	This work
		435	(2.6×10^3)	
		345(sh)		
		325	(9.2×10^3)	
$[\text{WO}(\text{S}_2)(\text{S}_2\text{CN} \text{C}_6\text{H}_5)_2]$	CH_2Cl_2	480	(1.9×10^3)	This work
		435	(2.7×10^3)	
		345(sh)		
		325	(9.4×10^3)	
$[\text{WS}(\text{S}_2)(\text{S}_2\text{CNBu}_2)_2]$	-	602		149
		394		
		360		
$[\text{WS}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	CH_2Cl_2	600	(3.4×10^3)	This work
		390	(10.8×10^3)	
		360	(9.8×10^3)	
$[\text{WS}(\text{S}_2)(\text{S}_2\text{CNPr}_2)_2]$	CH_2Cl_2	600	(3.2×10^3)	This work
		390	(10.4×10^3)	
		356	(9.3×10^3)	

..contd.

Table 4.7 (contd.)

1	2	3	4
$[\text{WS}(\text{S}_2)(\text{S}_2\text{CN} \text{C}_6\text{H}_4 \text{CN})_2]$	CH_2Cl_2	600 (2.8×10^3) 392 (8.6×10^3) 356 (7.4×10^3)	This work
$(\text{Et}_2\text{NH}_2)[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)]$	CH_2Cl_2	480 (0.8×10^3) 412 (1.3×10^3) 322 (4.4×10^3)	This work
$(\text{Pr}_2\text{NH}_2)[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNPr}_2)]$	CH_2Cl_2	475 (1.1×10^3) 408 (1.7×10^3) 325 (4.2×10^3)	This work
$[\text{WO}(\text{S}_2\text{CNET}_2)_2]$	CH_2Cl_2	400(sh) 340 (2.3×10^3)	This work
$[\text{WO}(\text{S}_2\text{CN} \text{C}_6\text{H}_4 \text{CN})_2]$	CH_2Cl_2	400(sh) 340 (2.1×10^3)	This work

Table 4.8 Electronic Spectral Data

Complex	Solvent	$\lambda_{\text{max}} (\epsilon)$ (nm)
$[\text{W}_2\text{O}_2(\mu-\text{s})_2(\text{s}_2\text{CNET}_2)_2]$	CH_2Cl_2	415 (0.2×10^3) 332 (1.5×10^3) 296 (7.6×10^3)
$[\text{W}_2\text{O}_2(\mu-\text{s})_2(\text{s}_2\text{CN} \text{C}_6\text{H}_4)_2]$	CH_2Cl_2	410 (0.8×10^3) 338 (3.8×10^3) 300 (14.6×10^3)
$[\text{W}_2\text{OS}(\mu-\text{s})_2(\text{s}_2\text{CNET}_2)_2]$	CH_2Cl_2	418 (0.7×10^3) 352 (4.4×10^3) 295 (27,400)
$[\text{W}_2\text{OS}(\mu-\text{s})_2(\text{s}_2\text{CN} \text{C}_6\text{H}_4)_2]$	CH_2Cl_2	422 (1.4×10^3) 352 (6.6×10^3) 297 (30.3×10^3)
$[\text{W}_2\text{S}_2(\mu-\text{s})_2(\text{s}_2\text{CNET}_2)_2]$	CH_2Cl_2	420 (2.2×10^3) 382 (6.5×10^3) 292 (30.1×10^3)

4.2.3 Magnetic Resonance Studies

^1H NMR Spectra

^1H NMR spectra of some of the complexes are reproduced in Figs. 4.3.1 to 4.3.4. Chemical shifts relative to TMS and assignments are presented in Table 4.9. The spectrum of $(\text{Et}_2\text{NH}_2)^+ \cdot [\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)_2]$ shows besides methyl and methylene protons, two sets of methylene protons at 3.4 and 3.85 δ ppm. The splitting of these methylene protons arising from diethylaminium cation is not properly understood.

The complex $[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)_2]$ differs from $[\text{WS}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)_2]$ only in containing a more electronegative atom at terminal position. This difference is clearly reflected by the expected chemical shifts of the protons in the ^1H NMR spectra. The general feature of these spectra are very much identical to those reported for $[\text{MoO}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)_2]$.⁶³

The ^1H NMR spectral data for $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$, $[\text{W}_2\text{OS}(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$ and $[\text{W}_2\text{S}_2(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$ show that the replacement of oxygen by sulfur causes downfield shift of both methyl as well as methylene protons. A similar trend has been observed in analogous molybdenum complexes.⁹⁷ An interesting difference between the spectrum of $[\text{Mo}_2\text{OS}(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$ and its tungsten analog, $[\text{W}_2\text{OS}(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$ is that the former complex gives doublet of the triplet whereas the tungsten analog shows doublet of the quartet.⁹⁷

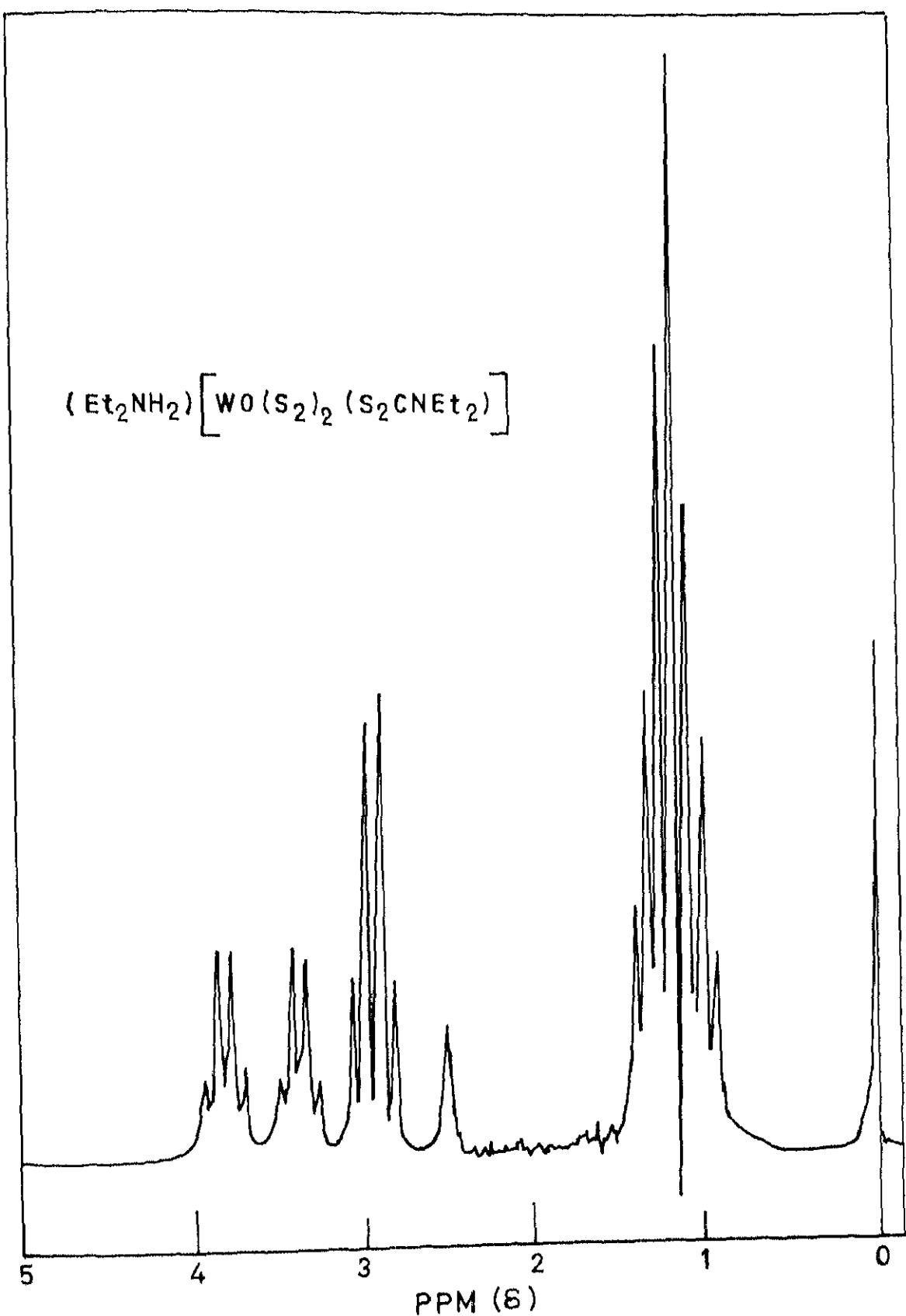
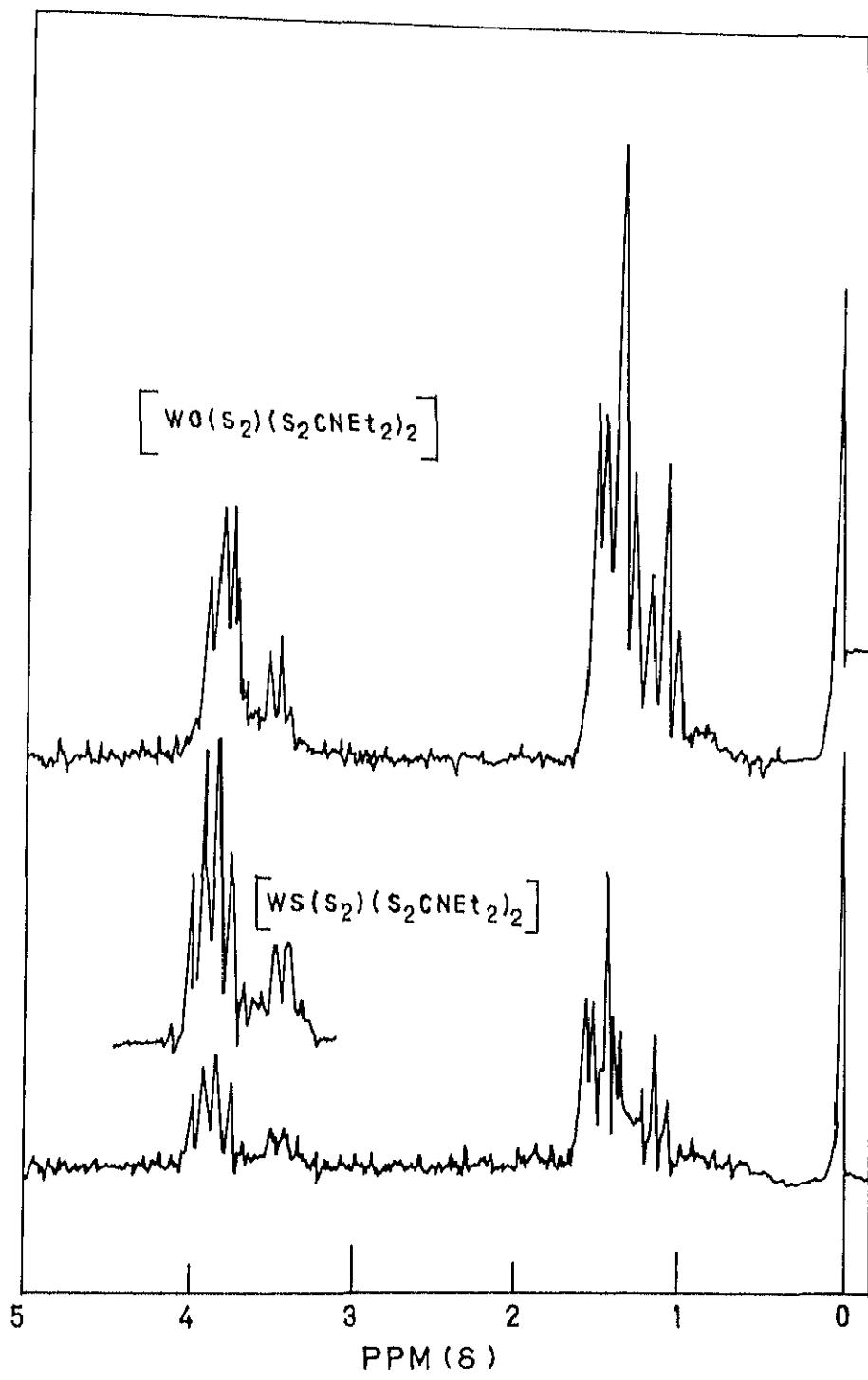


FIG. 4.3.1 1H NMR SPECTRUM

FIG 4.3.2 ^1H NMR SPECTRA

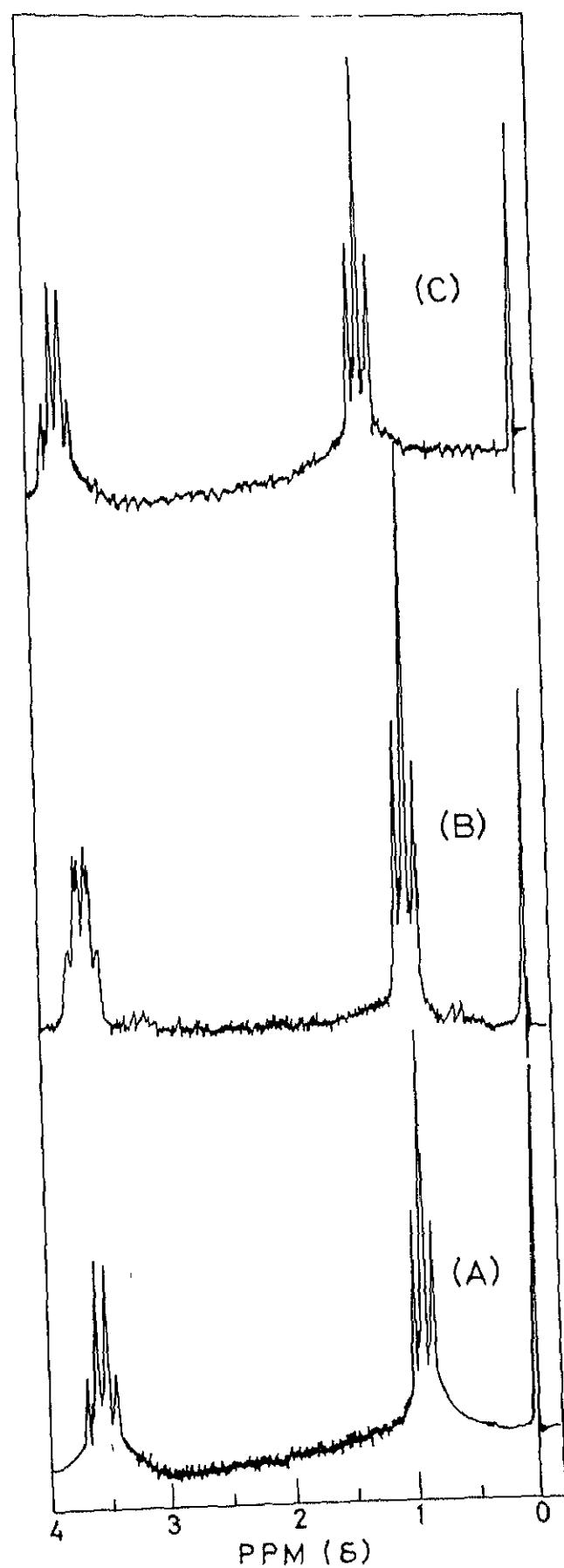


FIG. 4.3.3 ^1H NMR SPECTRA: (A) $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$; (B) $[\text{W}_2\text{OS}(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ and (C) $[\text{W}_2\text{S}_2^-(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ in $\text{C}_6\text{D}_5\text{N}$.

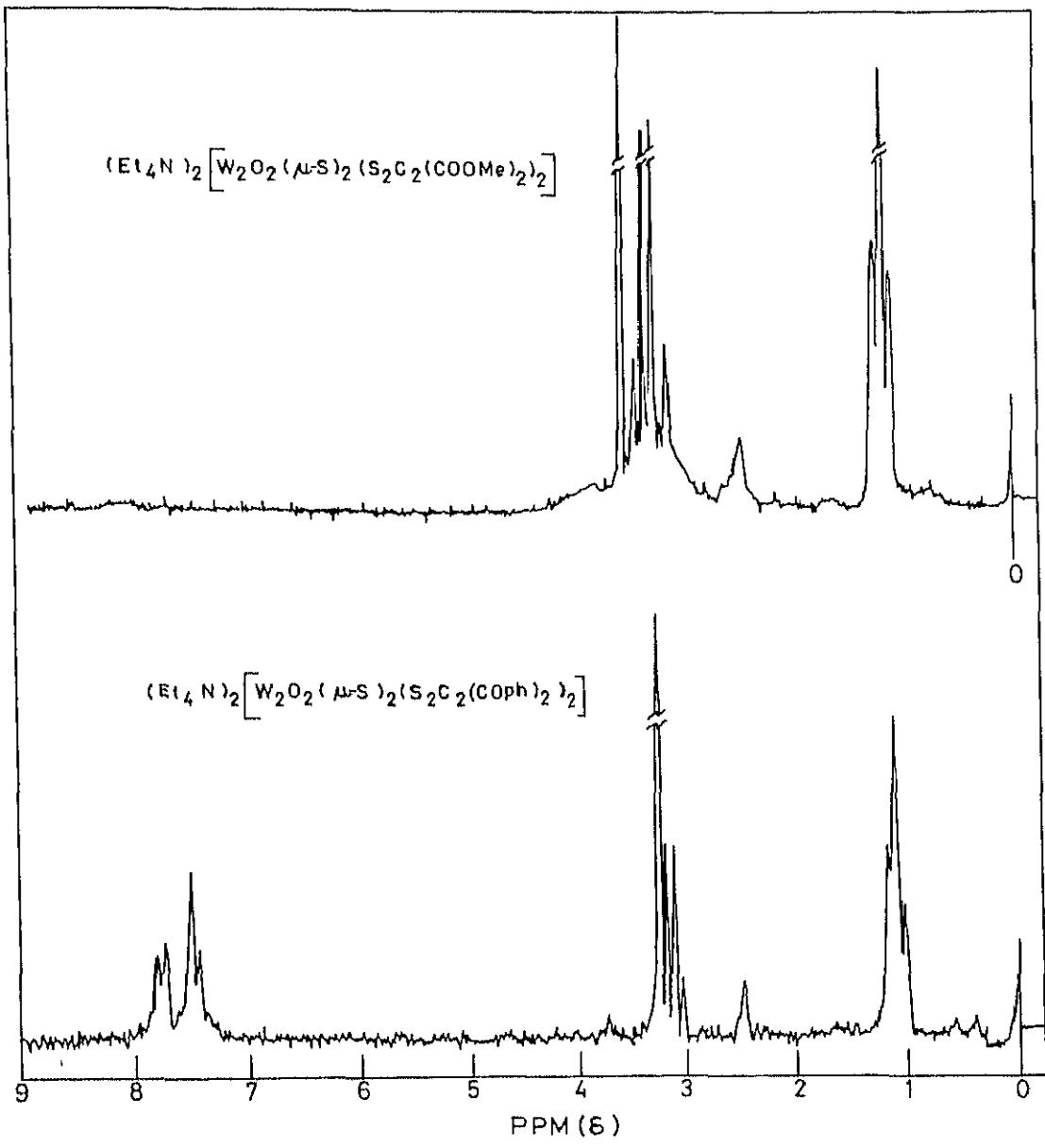
FIG 4 3 4 1H NMR SPECTRA

Table 4.9 ^1H NMR Spectral Data

Complex	Solvent	Absorption	δ (ppm)
1	2	3	
$(\text{Et}_2\text{NH}_2)[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)]$	DMSO-d_6	0.9-1.5 (tt, CH_3 , 12H) 2.95 (q, CH_2 , 4H) 3.4 (q, CH_2 , 2H) 3.85 (q, CH_2 , 2H)	
$[\text{MoO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	CDCl_3	1.41 (t) ³⁶ 1.45 (t) 3.97 (q) 4.02 (q)	
$[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	CDCl_3	1.1 (t, CH_3 , 3H) 1.21-1.61 (m, CH_3 , 9H) 3.48 (q, CH_2 , 4H) 3.61-4.0 (q, CH_2 , 4H)	
$[\text{WS}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	CDCl_3	1.18 (t, CH_3 , 3H) 1.26-1.68 (m, CH , 9H) 3.48 (q, CH_2 , 4H) 3.7-4.05 (q, CH_2 , 4H)	
$[\text{WO}(\text{S}_2)(\text{S}_2\text{CNPr}_2)_2]$	CDCl_3	0.66-1.15 (m, CH_3 , 6H) 1.5-2.1 (m, CH_3 , 6H) 3.41 (q, CH_2 , 4H) 3.73 (q, CH_2 , 12H)	

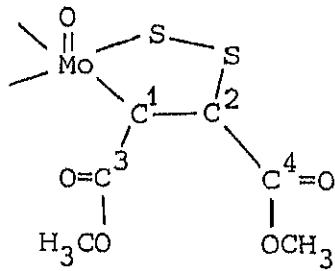
...contd.

Table 4.9 (contd.)

	1	2	3
$[\text{WS}(\text{S}_2)(\text{S}_2\text{CNPr}_2)_2]$		CDCl_3	0.66-1.2 (m, CH_3 , 6H) 1.5-2.1 (m, CH_3 , 6H) 3.3 (q, CH_2 , 4H) 3.72 (q, CH_2 , 12H)
$[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$		$\text{C}_5\text{D}_5\text{N}$	0.95 (t, CH_3 , 12H) 3.54 (q, CH_2 , 8H)
$[\text{W}_2\text{OS}(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$		$\text{C}_5\text{D}_5\text{N}$	0.98 (t, CH_3 , 12H) 3.62 (q, CH_2 , 8H)
$[\text{W}_2\text{S}_2(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$		$\text{C}_5\text{D}_5\text{N}$	1.08 (t, CH_3 , 12H) 3.74 (q, CH_2 , 8H)
$(\text{Et}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$	DMSO-d_6		1.11 (t, cation CH_3 , 24H) ⁷⁸ 3.13 (q, cation CH_2 , 16H) 3.72 (s, ester, 6H) 3.77 (s, ester, 6H)
$(\text{Et}_4\text{N})_2[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$	DMSO-d_6		1.14 (t, cation, CH_3 , 24H) 3.28 (q, cation CH_2 , 16H) 3.5 (s, ester, 12H)
$(\text{Et}_4\text{N})_2[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{C}_2(\text{COPh})_2)_2]$	DMSO-d_6		1.1 (t, cation CH_3 , 24H) 3.2 (q, cation CH_2 , 16H) 7.2-8.0 (m, O-Ph, 20 H)
$(\text{Et}_4\text{N})_2[\text{W}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$	DMSO-d_6		1.16 (t, cation CH_3 , 24H) 3.23 (q, cation CH_2 , 16H) 7.2-8.0 (m, O-Ph, 30H)

s = singlet, t = triplet, q = quartet, m = multiplet.

^1H NMR spectroscopy was found to be very helpful in understanding the mode of insertion of acetylene in $(\text{Et}_4\text{N})_2[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]$. In the case of its molybdenum analog, the insertion was found to take place across Mo-S bond, as two singlets at 3.72 and 3.77



for $-\text{OCH}_3$ attached to two different carbon atoms, C-3 and C-4 were observed. However, ^1H NMR spectrum of $(\text{Et}_4\text{N})_2[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ shows only a singlet in this region, suggesting the identical nature of two methoxy groups in the resulting complex. On the basis of the above observations, it has been suggested that the insertion takes place across S-S bond and dithiolene ligated complex is formed. Further support to this proposition comes from ^{13}C NMR studies (vide infra).

^{13}C NMR Spectra

^{13}C NMR studies were carried out to understand the nature of insertion reaction of the activated acetylene, DBA, with $\{\text{W}\text{--S}\}$ moiety. There are reports that the insertion may take place across Mo-S or S-S bond in molybdenum-sulfur complexes with the formation of vinyl disulfide or dithiolene coordinated complexes.

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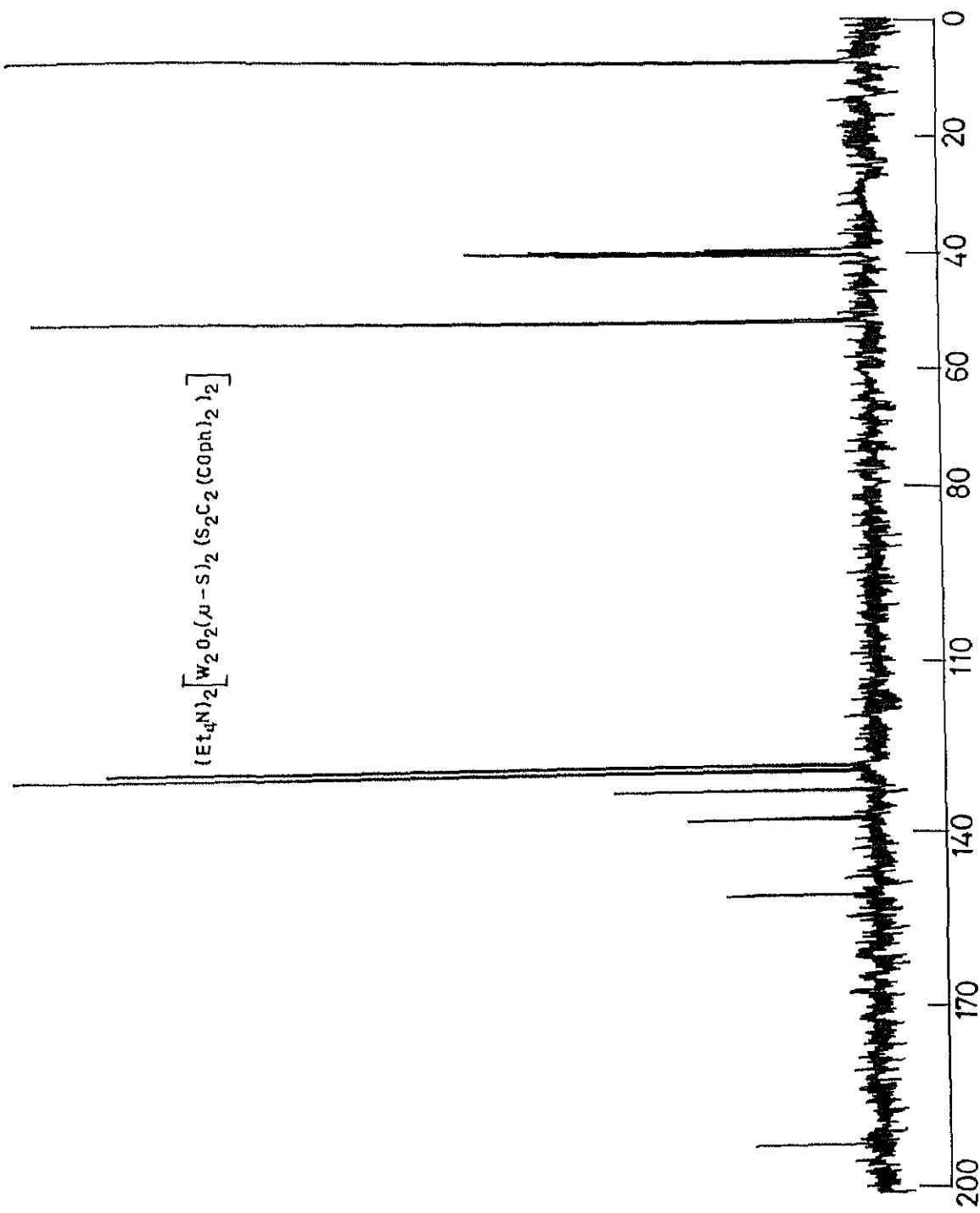
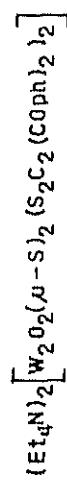


FIG 4.35 ^{13}C NMR SPECTRUM

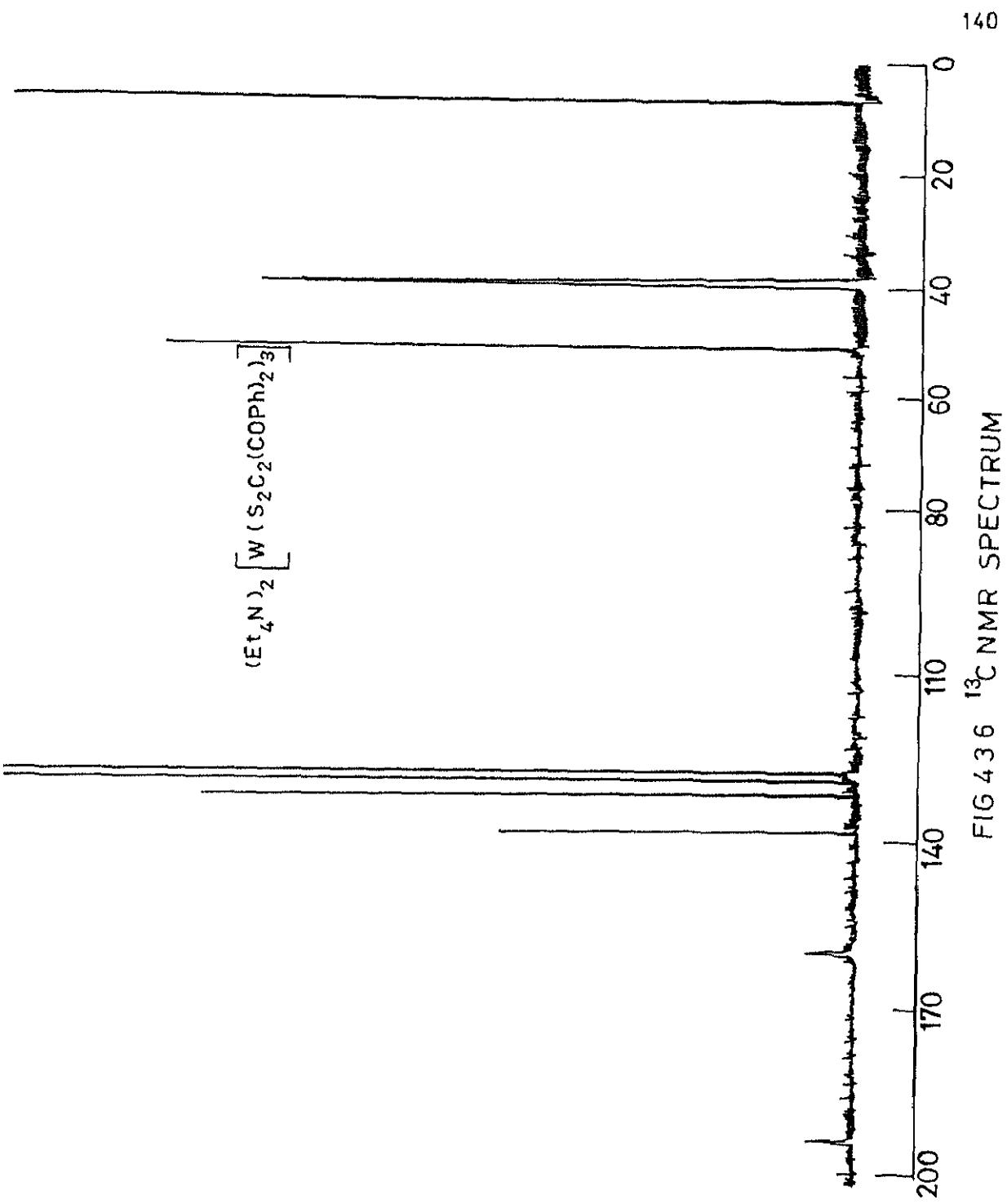
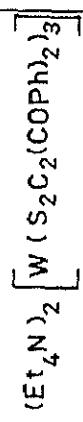


FIG 436 ^{13}C NMR SPECTRUM

Table 4.10 ^{13}C NMR Chemical Shifts

Complex	Cation (CH_2 , (CH_3)	DMSO	Ph	$\text{C}=\text{C}$	CO	Reference
$(\text{Et}_4\text{N})_2[\text{MoO}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]$	6.96 51.41	38.84- 40.63	137.56 132.11	148.53	193.92	137
$(\text{Et}_4\text{N})_2[\text{W}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$	6.96 51.41	38.86- 40.11	138.45 131.56	159.89	193.91	This work
$(\text{Et}_4\text{N})_2[\text{W}_2\text{O}_2(\mu-\text{s})_2(\text{S}_2\text{C}_2(\text{COPh})_2)_2]$	6.97 51.43	39.08- 39.91	137.45 132.35	150.44	193.93	This work
				129.02		
				127.97		

The complex $(Et_4N)_2[W_2O_2(\mu-S)_2(S_2C_2(COPh)_2)_2]$ shows ^{13}C NMR spectrum which is very much similar to the spectra recorded for $(Et_4N)_2[MoO(S_2C_2(COPh)_2)_2]^{137}$ and $(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$. These spectra are reproduced in Figs. 4.3.5 and 4.3.6 and chemical shifts relative to TMS are tabulated in Table 4.10. By analogy with other bis- and tris-dithiolene complexes of molybdenum and tungsten, prepared by insertion reactions ^{13}C NMR data can be interpreted. The ^{13}C NMR spectral data of $(Et_4N)_2[W_2O_2(\mu-S)_2(S_2C_2(COPh)_2)_2]$ and $(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$ are almost identical, suggesting the presence of similar ligands in both the cases. This indicates clearly that the mode of insertion in $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ is across S-S bond of $\begin{array}{c} S \\ | \\ \{W \} \\ | \\ S \end{array}$ moiety, contrary to the molybdenum analog.⁶⁸

ESR Spectra

All the complexes described in this dissertation are diamagnetic and ESR inactive. However, during the formation of $[WO(S_2)(S_2CNET_2)_2]$ and $[WS(S_2)(S_2CNET_2)_2]$, ESR active species could be identified. The ESR spectra recorded during the formation of these complexes are reproduced in Figs. 4.3.7 and 4.3.8. Hyperfine splitting due to ^{183}W ($I = 1/2$) is not readily detected though the natural abundance of this isotope is 14.28 %. ^{153}W This is probably because of the high $\langle g \rangle$ value for this type of systems. The species under investigation give ESR signal which shows superhyperfine splitting suggesting the presence of two protons in the vicinity of the W(V) center. ESR studies have been

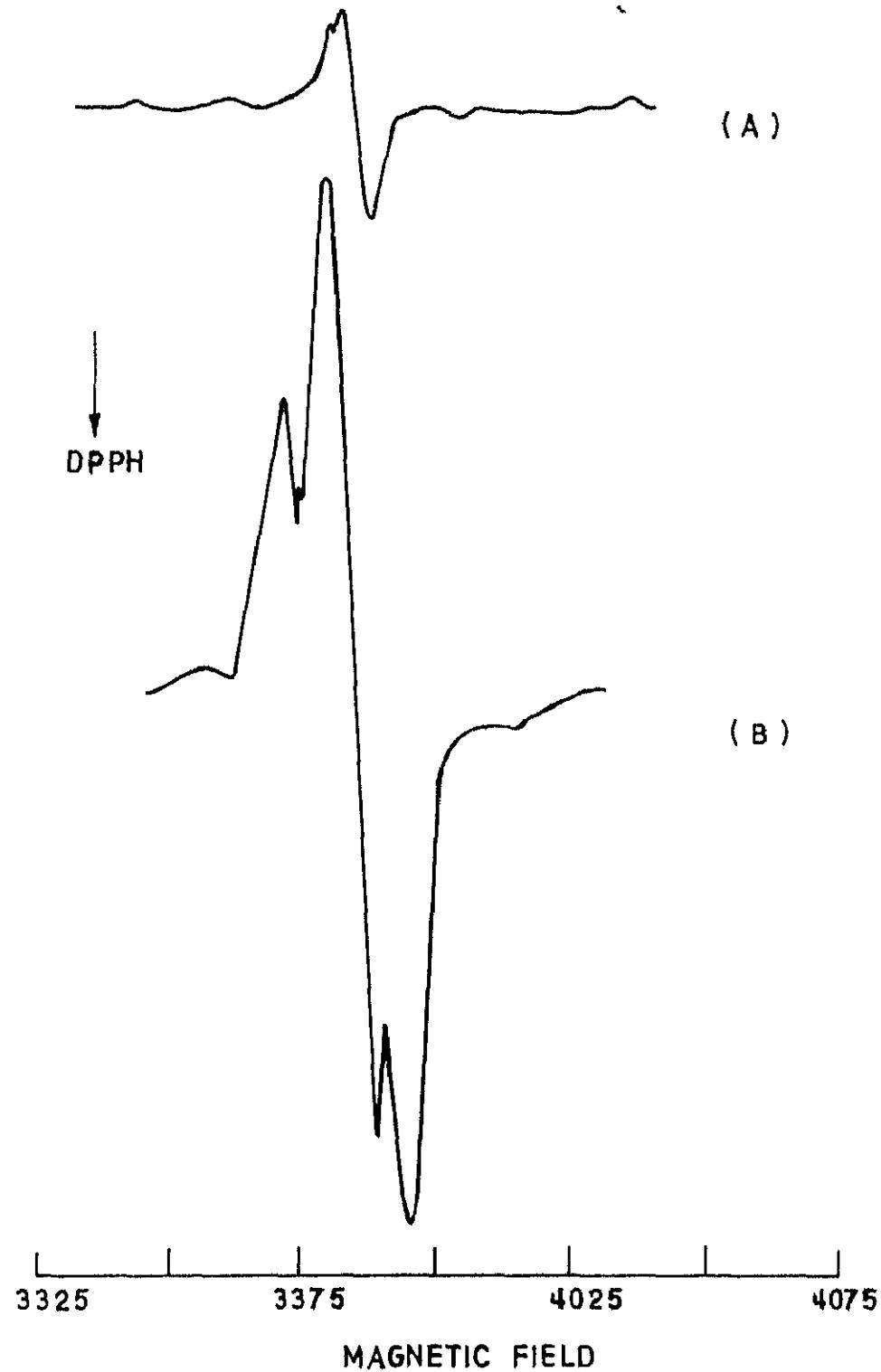


FIG. 4.3.7 ESR SPECTRA

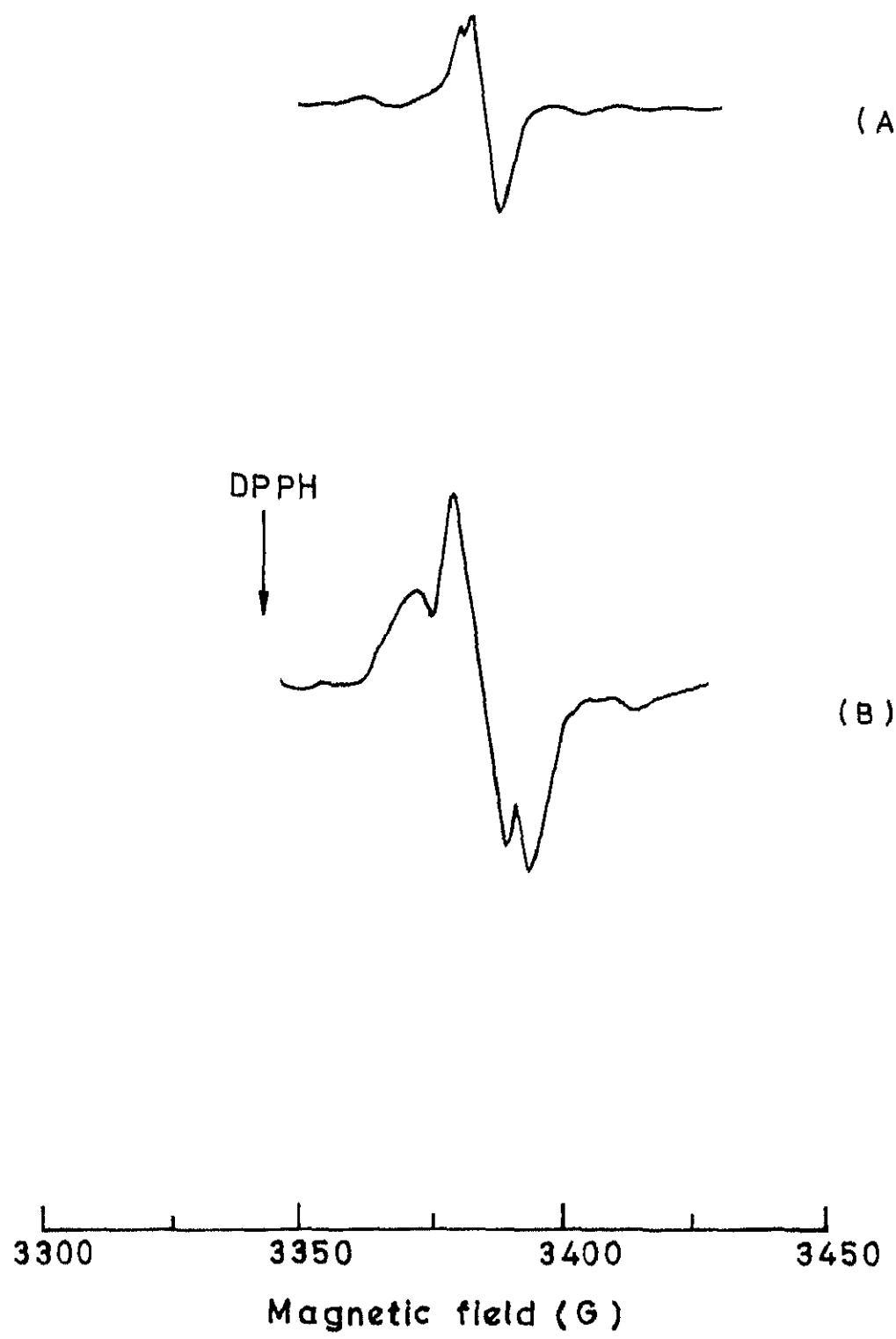


FIG.4.3.8 ESR SPECTRA

found to be very helpful in determining the path of the reaction. When CS_2 is added to a DMF solution of $(\text{Et}_2\text{NH}_2)_2\text{WOS}_3$ or $(\text{Et}_2\text{NH}_2)_2\text{WS}_4$ at room temperature in air, the ESR signal starts appearing within 5 min which gains maximum intensity after 8 hr and then starts decaying and ultimately disappears after 20 hr. The super-hyperfine interaction with two protons is seen in the ESR spectrum suggesting the presence of an intermediate species containing $\{\text{W}^{\text{V}}(\text{SH})_2\}$ moiety. A noteworthy feature of these spectra is that the $\langle g \rangle$ values remain constant throughout, clearly indicating the involvement of only one $\text{W}(\text{V})$ species in this reaction. On the basis of the above observations and the identification of the superoxide ion radical during the course of the reaction, a probable mechanism has been suggested (vide supra, Eqn. 4.1).

4.2.4 C.V. Studies

Some of the complexes synthesized in the present study are the products of induced electron transfer reactions. Thus, it is important to study the electrochemical behaviour of some of these complexes. The cyclic voltammetric (C.V.) study of these complexes were carried out in CH_3CN and cyclic voltammograms are reproduced in Figs. 4.5.1 to 4.5.3. The relevant data are given in Table 4.11. The complex $(\text{Et}_2\text{NH}_2)[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)]$ which is presumed to be formed by a series of electron transfer reactions (vide infra), shows an irreversible redox behaviour. The low oxidation potential value is suggestive of facile redox capability of the attached ligand, persulfide or dithiocarbamate on oxidation. The

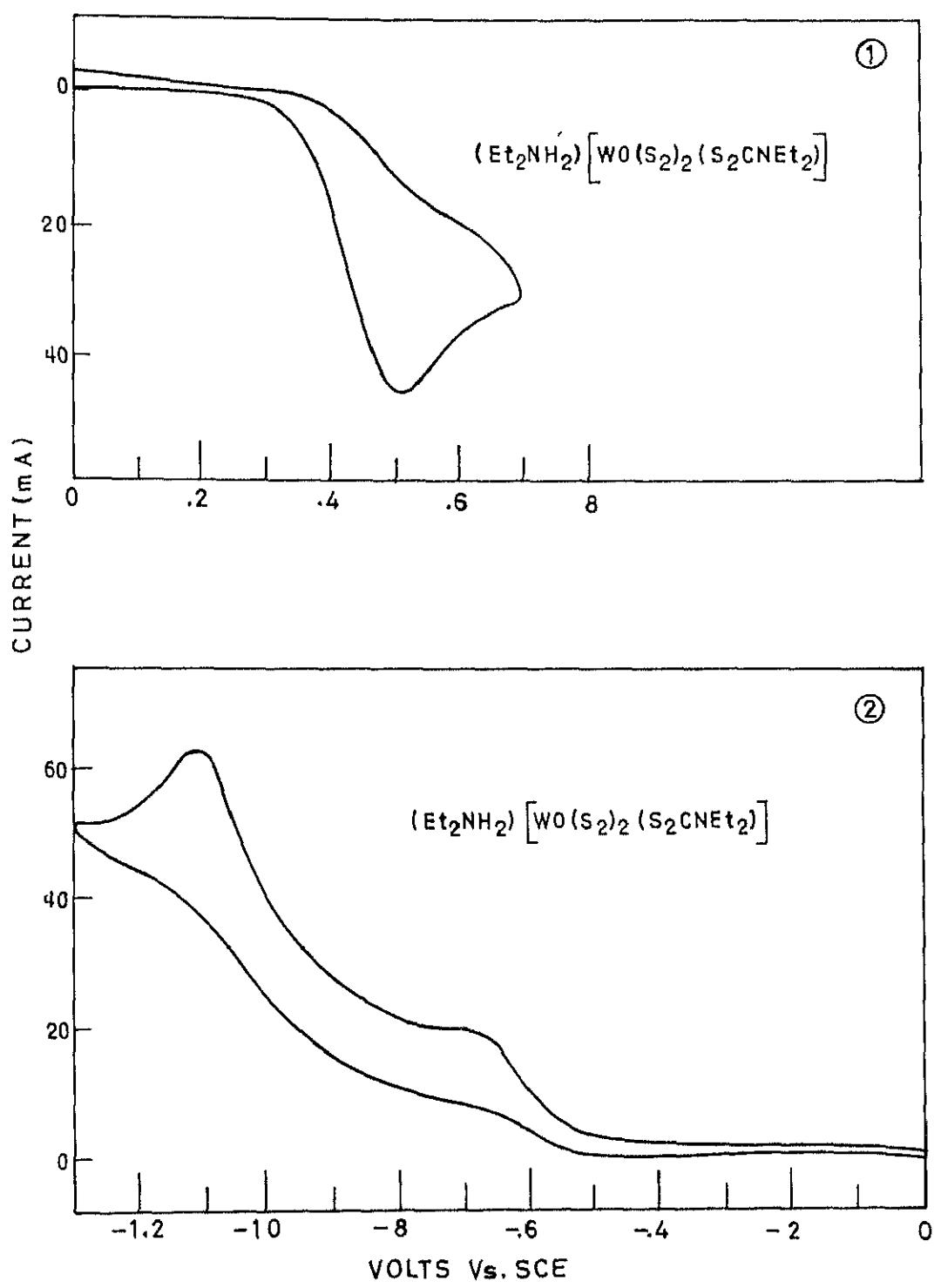


FIG. 4.41 CYCLIC VOLTAMMOGRAM 1. OXIDATION 2. REDUCTION
SCAN RATE 50 mV s^{-1}

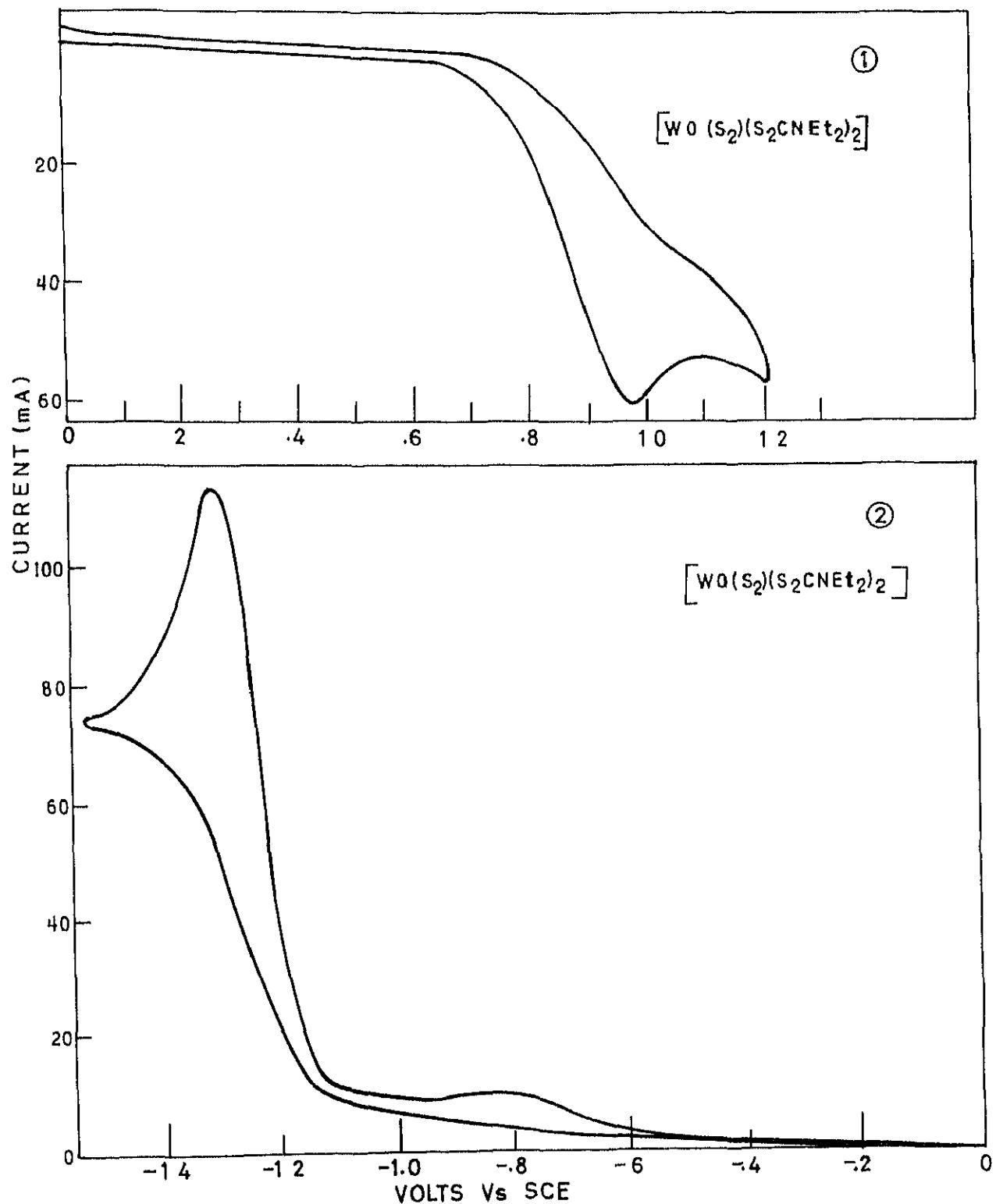


FIG 4.4.2 CYCLIC VOLTAMMOGRAM. 1 OXIDATION 2 REDUCTION
SCAN RATE 50 mVs^{-1}

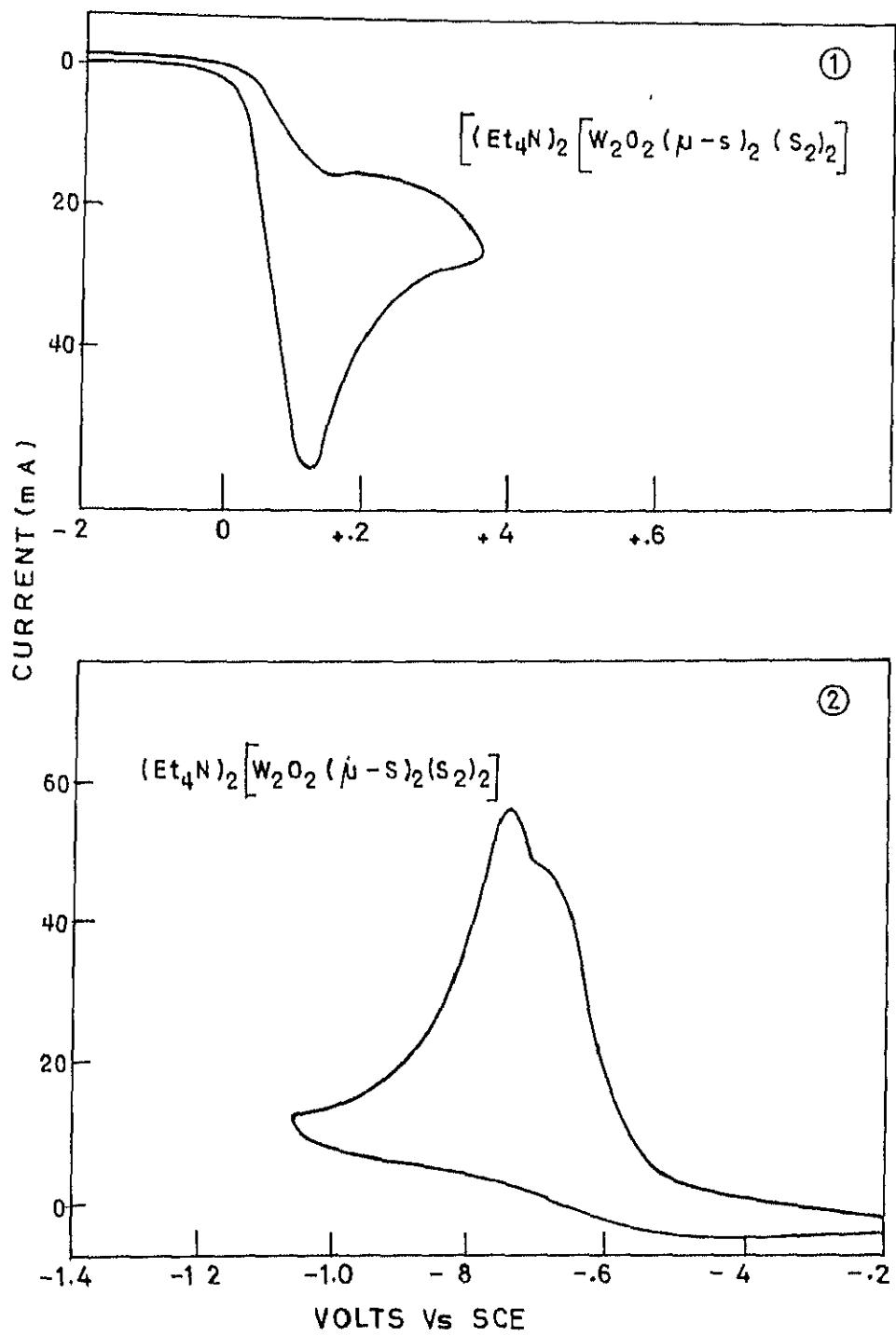


FIG. 4 4.3 CYCLIC VOLTAMMOGRAM . 1. OXIDATION 2. REDUCTION
SCAN RATE 50 mV s^{-1}

Table 4.11 Electrochemical Redox Potentials ^{*} vs SCE

Complex	Concen- tration (CH ₃ CN) mVs ⁻¹	Scan rate mVs ⁻¹	Oxidation		Reduction	
			Potential (V)	Current (mV)	Potential (V)	Current (mA)
(Et ₂ NH ₂) ₂ [WO(S ₂) ₂ (S ₂ CNEt ₂)]	1.5x10 ⁻³	50	+0.50	47	-0.54	26
					-1.00	70
[WO(S ₂) ₂ (S ₂ CNEt ₂) ₂]	1.05x10 ⁻³	50	+0.98	60	-0.80	10
					-1.31	114
(Et ₄ N) ₂ [W ₂ O ₂ (μ-S) ₂ (S ₂) ₂]	1.19x10 ⁻³	50	+0.12	58	-0.72	60

* 0.1 M (Et₄N)ClO₄ was used as supporting electrolyte.

reduction potential value suggests the capability of the metal center and/or persulfide ligand to undergo reduction. The irreversible nature of these C.V. studies proved that the intermediate species preceded by this compound is entirely different.

A comparison of the cyclic voltammogram of $(Et_2NH_2)^- [WO(S_2)_2(S_2CNET_2)]$ and $[WO(S_2)(S_2CNET_2)_2]^{2-}$ suggests that the redox stability increases with the substitution of $(S_2)^{2-}$ by $(S_2CNET_2)^-$ in such systems. For $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ the low oxidation potential values suggest the instability of this compound in oxidizing environment. We have also observed that the solution of this compound under aerial exposure gets oxidized slowly.

4.2.5 X-Ray Studies

X-Ray Photoelectron Spectra (XPS)

X-ray photoelectron spectroscopy can help to measure the core electron energies of elements in these complexes. This technique can also help to estimate the charge distribution on the various atoms of the complex. Some representative examples of the complexes described here, were subjected to this study and the spectra are reproduced in Figs. 4.5.1 to 4.5.6. The binding energies of tungsten and sulfur are tabulated in Table 4.12. For a comparative study XPS data of elemental sulfur, $[Mo_2O_2(\mu-S)_2(S_2)_2]^{2-}$, WO_4^{2-} , WS_4^{2-} and metallic tungsten are also incorporated in this table. The S(2p) binding energies in these

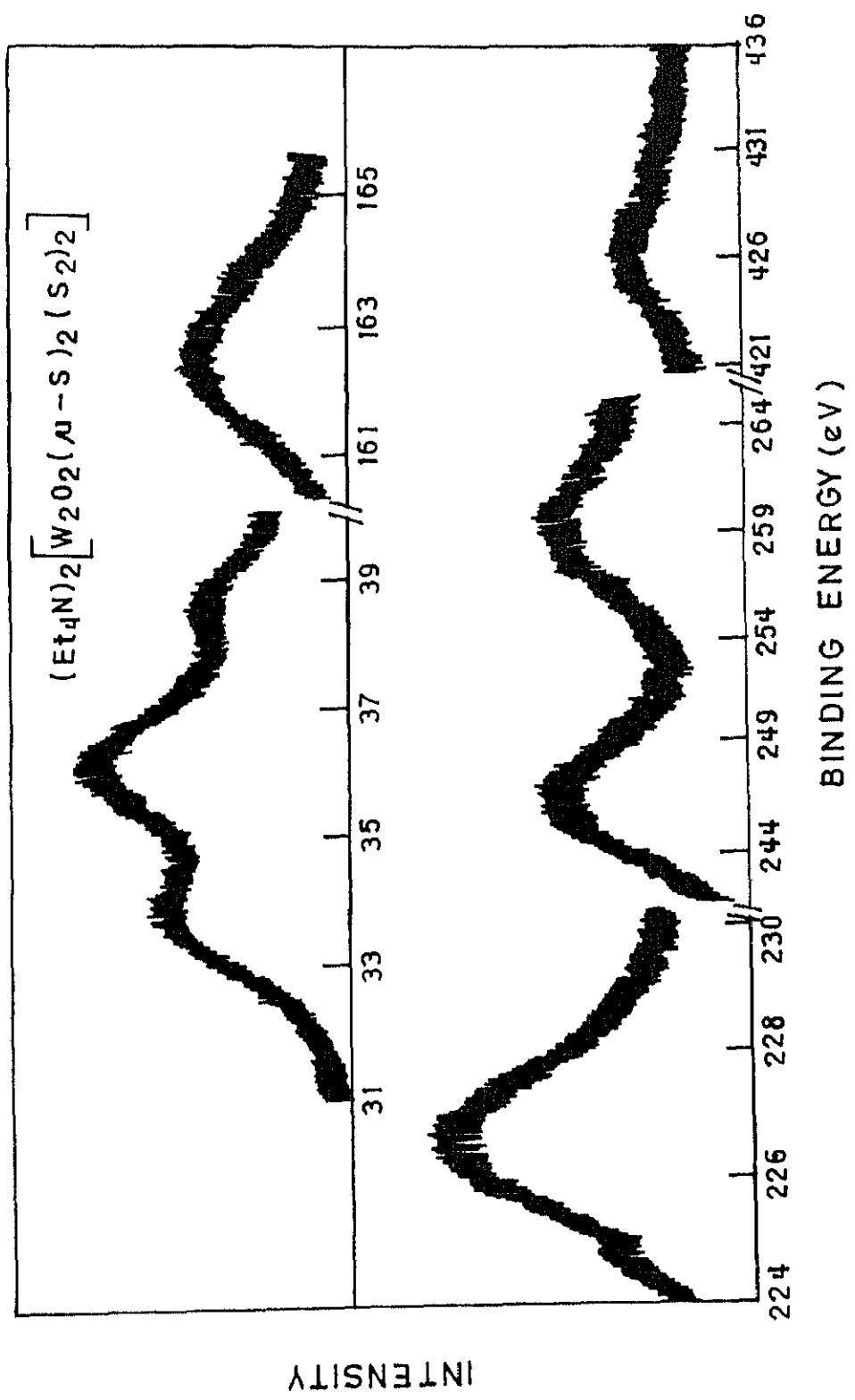
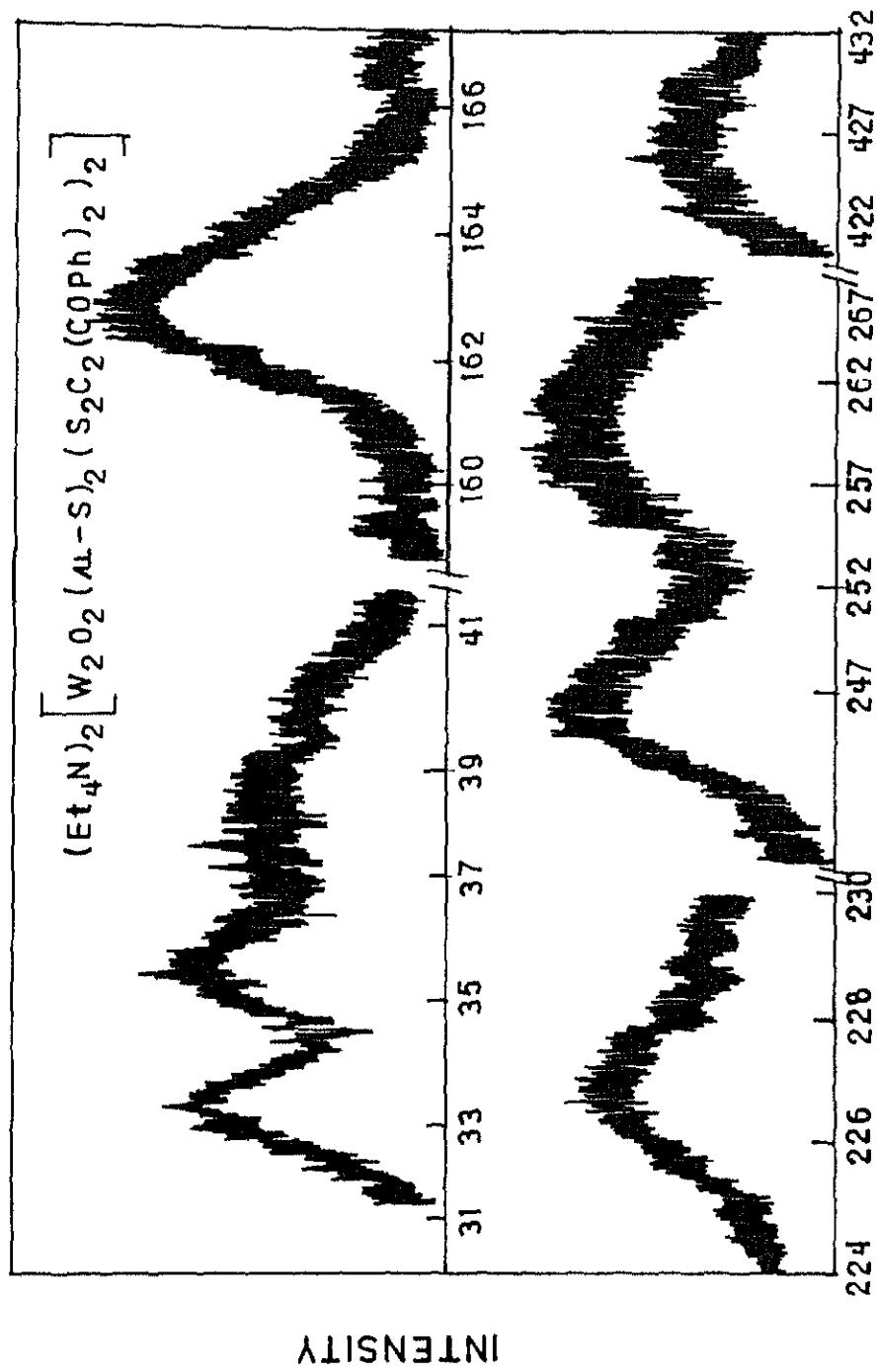


FIG. 4.5.1

FIG. 4.5.2

BINDING ENERGY (eV)



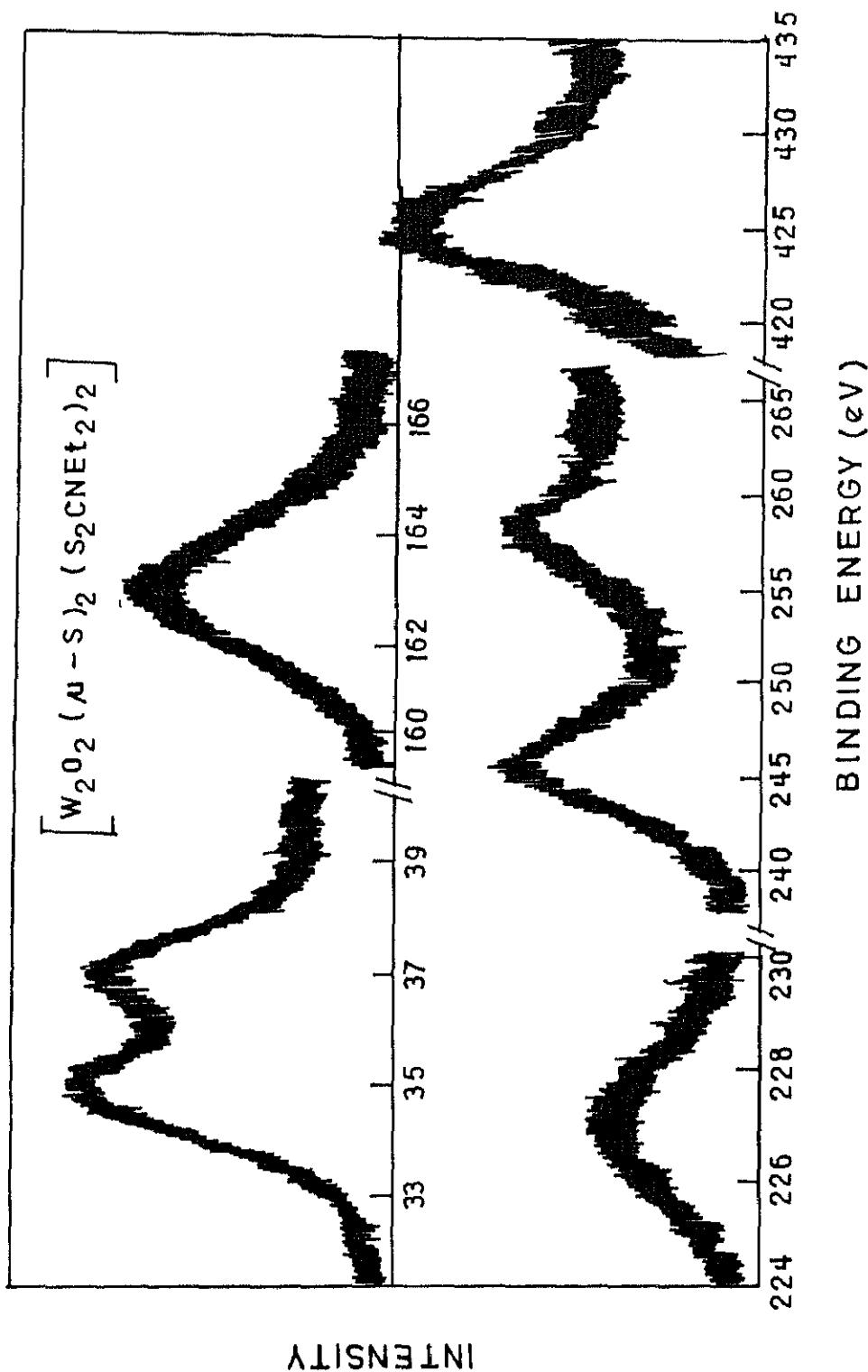


FIG 4.5.3

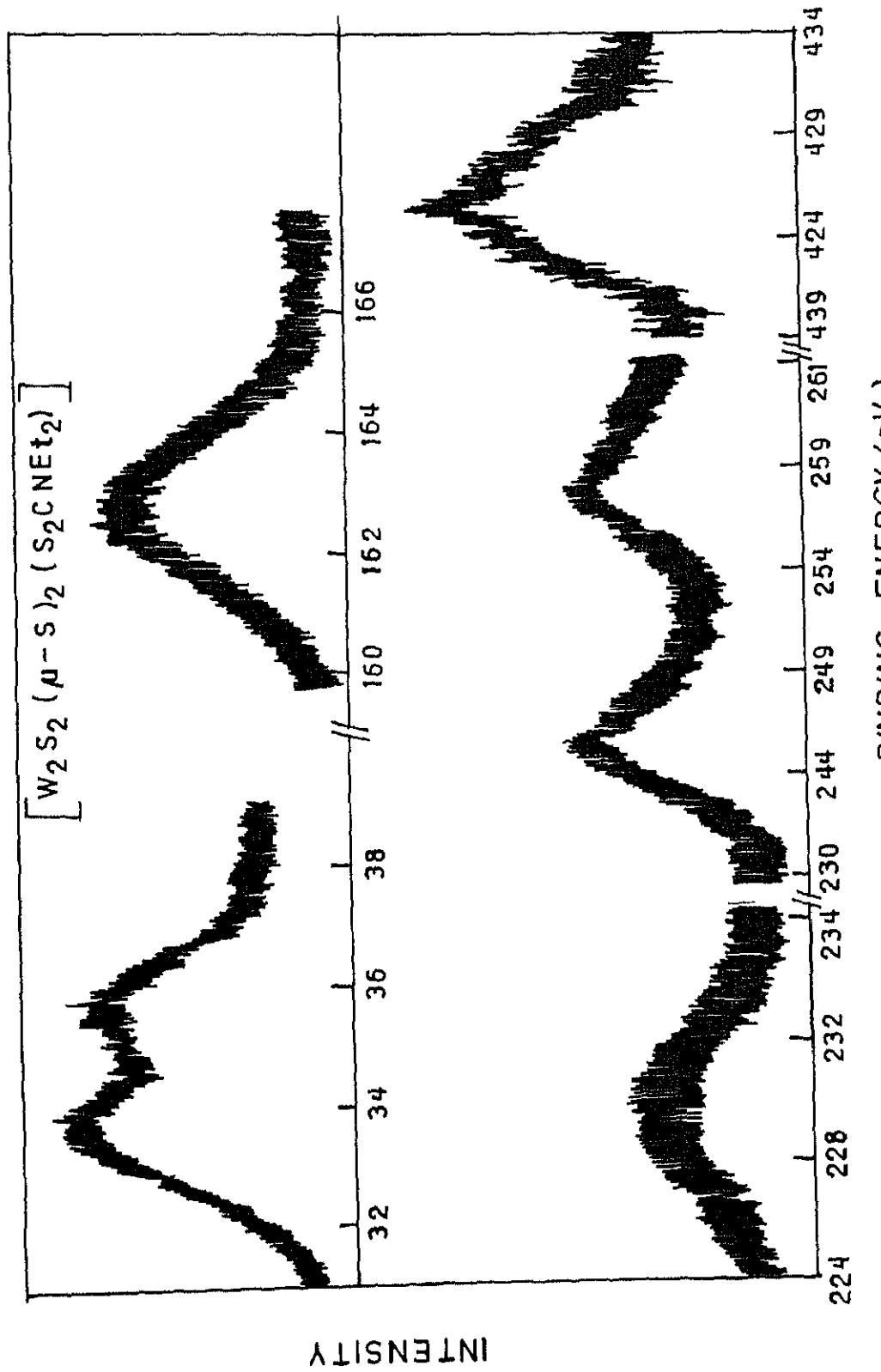


FIG 4.5.4

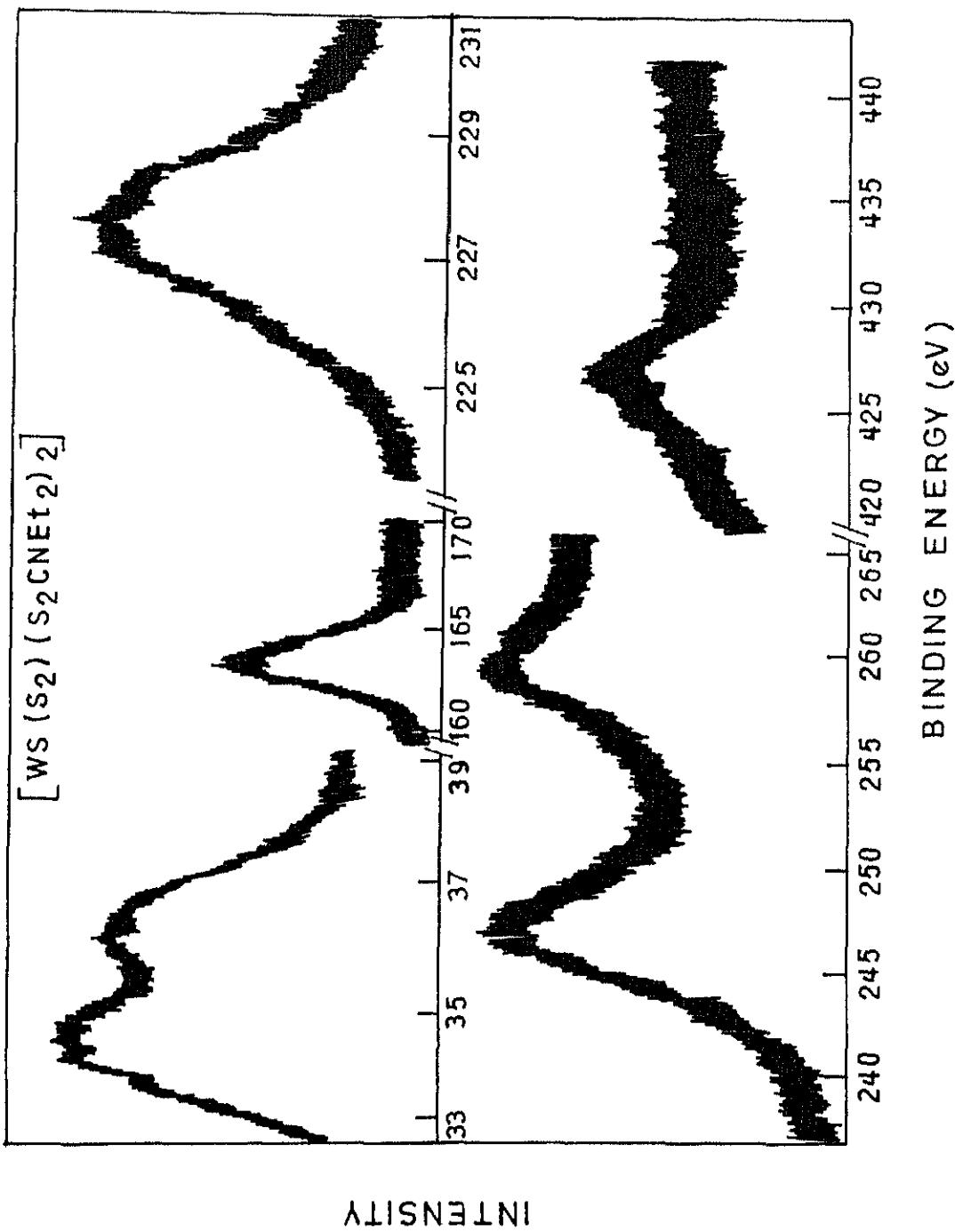


FIG 4.5.5

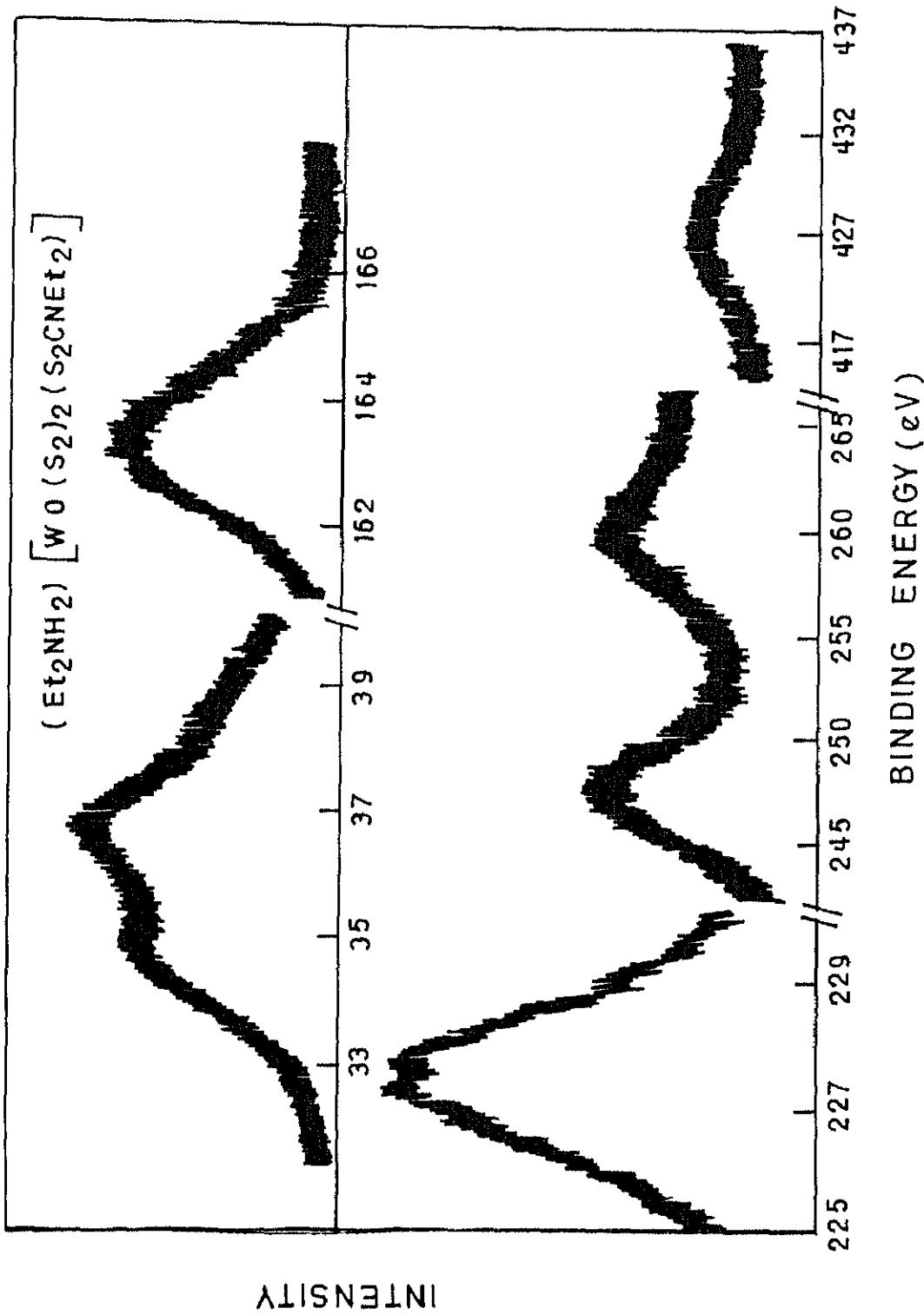


FIG. 4.5.6

complexes containing sulfur, compared to that of elemental sulfur, clearly demonstrate that the sulfur present either in the form of sulfido, persulfido, thiocarbamato or dithiolene, contain formal negative charge.

For the complex ion, $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$, the S(2p) and S(2s_{1/2}) values are more negative compared to the corresponding molybdenum analog, $[\text{Mo}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$. When persulfido ligand is replaced by thiocarbamato or dithiolene as in complexes $[\text{W}_2\text{O}_2(\mu-\text{S})(\text{S}_2\text{CNET}_2)_2]$ and $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{C}_2(\text{COPh})_2)_2]^{2-}$, the S(2p) and S(2s_{1/2}) values remain almost unchanged. However, the FWHM for S(2p) in these complexes differ. For the dithiolene derivative the lowest FWHM value (2.6 e.V.) suggests that the bridged sulfido ligand and dithiolene ligand mix so profoundly that the individual identity of these two different types of sulfur atoms is lost. This can be further appreciated by viewing the FWHM of S(2p) in $\text{S}_2\text{C}_2(\text{CN})_2^{2-}$ which is 2.7 e.V. For the other two complexes, $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$ and $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$, FWHM values suggest that in principle deconvolution of this band is possible and S(2p) binding energies for bridged sulfido, persulfido, and thiocarbamato ligand can be deduced following the procedure adopted by Siegbahn.¹⁵⁴ For $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$ the broad band for S(2p) binding energy when resolved gave two sets of S(2p) binding energies in the ratio 1:2 at 163.3 and 162.0 e.V. Similarly the band for $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$ on resolution gave S(2p) binding energies at 163.1 and 163.5 e.V. On the basis of these values, the S(2p) binding energies for bridged sulfido ligand is assumed

to occur in the range 163.1 - 163.3 e.v. in these complexes. When there are three different types of sulfur atoms attached to tungsten, for example, in $[W_2S_2(\mu-S)_2(S_2CNET_2)_2]$ the S(2p) binding energy band is very broad (FWHM 3.06). This extra broadness compared to the corresponding oxo complex, $[W_2O_2(\mu-S)_2(S_2CNET_2)_2]$, is accounted for the presence of an additional sulfur atom at a terminal position. In case of mononuclear complexes, $[WS(S_2)(S_2CNET_2)_2]$ & $[WO(S_2)_2(S_2CNET_2)]^-$ the S(2p) binding energy band is very narrow. The low FWHM values in these cases suggest that the mixing of different types of sulfur atoms is so effective that any distinction among them is not possible.

The $W(4f_{7/2})$ and $W(4f_{5/2})$ binding energies of these complexes show the expected trend. The values are higher for the complexes where the formal oxidation state is VI. Comparison of these W(VI) complexes with WO_4^{2-} suggest more electron density on tungsten in hepta-coordinated species, $[WO(S_2)_2(S_2CNET_2)]^-$ and $[WS(S_2)(S_2CNET_2)_2]$. Taking metallic tungsten in zero oxidation state, no meaningful correlation can be made. Any discrepancy in these values may be due to different standardization procedure. However, in the present study, a general correlation can definitely be made. The expected trend is also reflected in $W(4d_{5/2})$, $W(4d_{3/2})$ and $W(4p_{3/2})$ binding energies of the complexes discussed here (Table 4.12).

Table 4.12. Binding Energy (e.v.)

Complex	W(4f _{7/2})	W(4f _{5/2})	S(2p) (FWHM)	S(2s _{1/2})	W(4d _{5/2})	W(4d _{3/2})	W(4p _{3/2})	Ref.
Mo ₂ O ₂ (μ-S) ₂ (S ₂) ₂] ²⁻	-	-	164.2	-	-	-	-	157
N ₂ ^V O ₂ (μ-S) ₂ (S ₂) ₂] ²⁻	33.9	36.1	162.6 (2.92)	226.7	246.7	260.6	426.9	This work
N ₂ ^V O ₂ (μ-S) ₂ (S ₂ C ₂ (COPh) ₂) ₂] ²⁻	33.4	35.6	162.7 (2.60)	226.8	246.7	259.0	425.7	This work
N ₂ ^V O ₂ (μ-S) ₂ (S ₂ CNET ₂) ₂] ²⁻	33.9	36.1	163.3 (2.87)	227.0	245.7	259.4	426.0	This work
N ₂ ^V S ₂ (μ-S) ₂ (S ₂ CNET ₂) ₂] ²⁻	33.6	35.7	162.8 (3.06)	227.0	245.2	258.0	426.3	This work
Mo ^{VI} O(S ₂)(S ₂ CNET ₂) ₂] ²⁻	-	-	163.2	227.1	-	-	-	69, 86
N ^{VI} O(S ₂) ₂ (S ₂ CNET ₂) ₂] ²⁻	34.3	36.3	162.8 (2.60)	226.9	246.8	258.9	426.3	This work
N ^{VI} S(S ₂ CNET ₂) ₂] ²⁻	34.6	37.3	163.2 (2.60)	227.6	246.9	259.4	426.4	This work
S ₂ [W ^{VI} O ₄] ²⁻	37.9	39.7	-	-	249.0	262.3	-	155
S ₂ [W ^{VI} S ₄] ²⁻	35.9	37.7	162.8	-	247.6	259.8	-	155
(fol1)	34.0	37.0	-	-	246.0	259.0	426.0	157

X-Ray Powder Diffractograms

X-ray powder diffractograms of $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$ and $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$ (Figs. 4.5.7 and 4.5.8) were recorded to make a comparison with the corresponding molybdenum complexes. The powder pattern of these compounds was found to be similar to those of their molybdenum analogs. This suggests that $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]^{2-}$ and $[\text{W}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$ could be isostructural to their molybdenum analogs.^{32,158} A comparison of X-ray powder pattern of $[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$ with $[\text{WS}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$ (Fig. 4.5.9) suggests that these two are also isostructural.

X-Ray Crystal Structure of $(\text{Et}_2\text{NH}_2)[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)]$

Crystal data of $(\text{Et}_2\text{NH}_2)[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)]$ are presented in Tables 4.13 - 4.17. The structure with bond distances (Fig. 4.5.10) shows that W(VI) is seven coordinate with a terminal oxygen, two edge-bound S_2^{2-} and one chelated $(\text{S}_2\text{CNET}_2)^-$ ligand arranged in a pentagonal bipyramidal polyhedron. The S_2^{2-} ligands and one sulfur of the dithiocarbamate ligand lie in the equatorial plane. Oxygen and the second sulfur of the dithiocarbamate ligand occupy the axial positions. It is interesting to note that the tungsten atom lies 0.32 Å above the mean plane through S1-S5 (Fig. 4.5.10). Another feature worth noting is that W-S₆ (sulfur of the dithiocarbamate unit) trans to oxygen is (2.605 Å) significantly longer than the equatorial W-S₅ bond (2.510 Å).

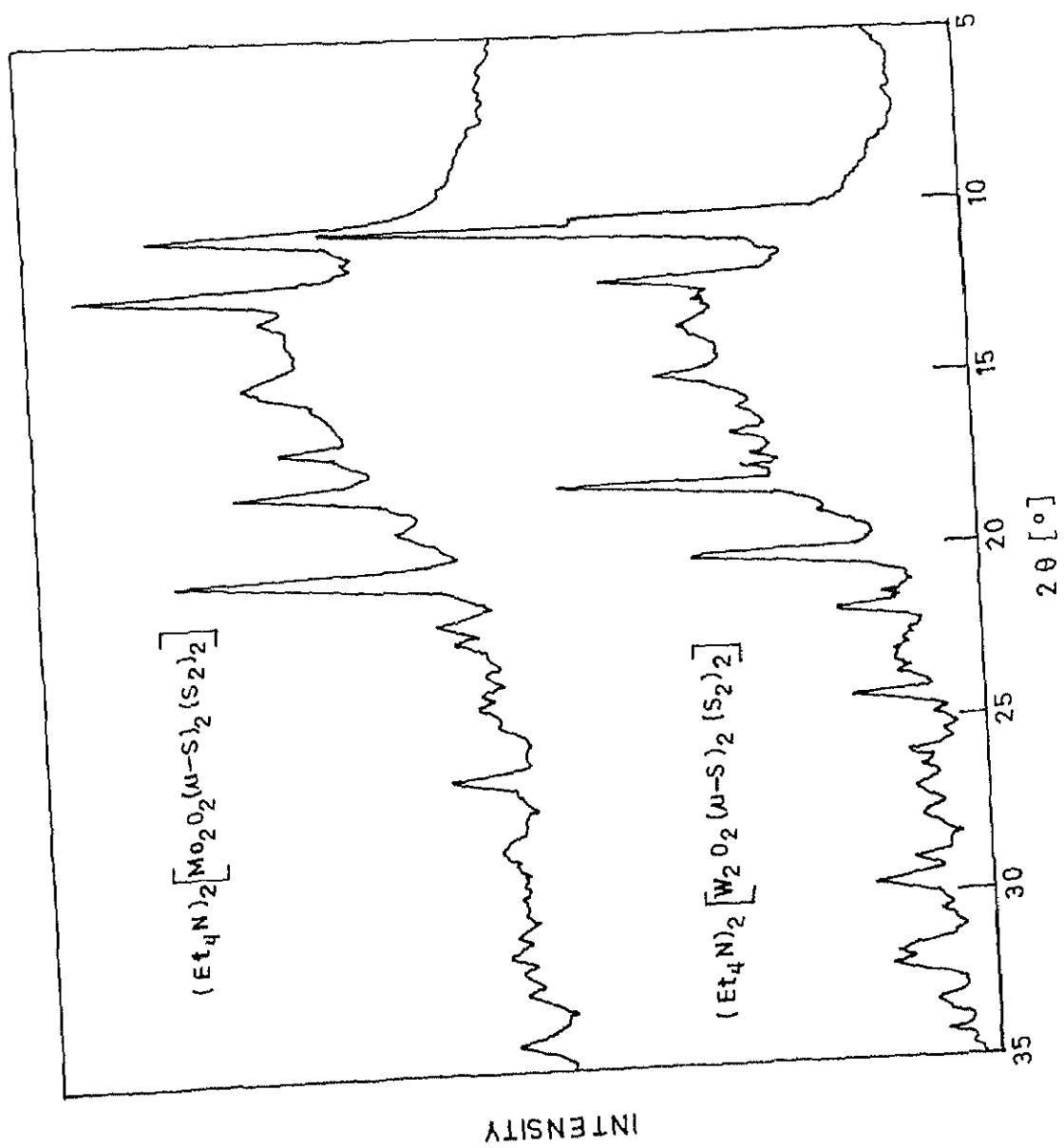


FIG 4.5.7 X-RAY POWDER DIFFRACTOGRAMS

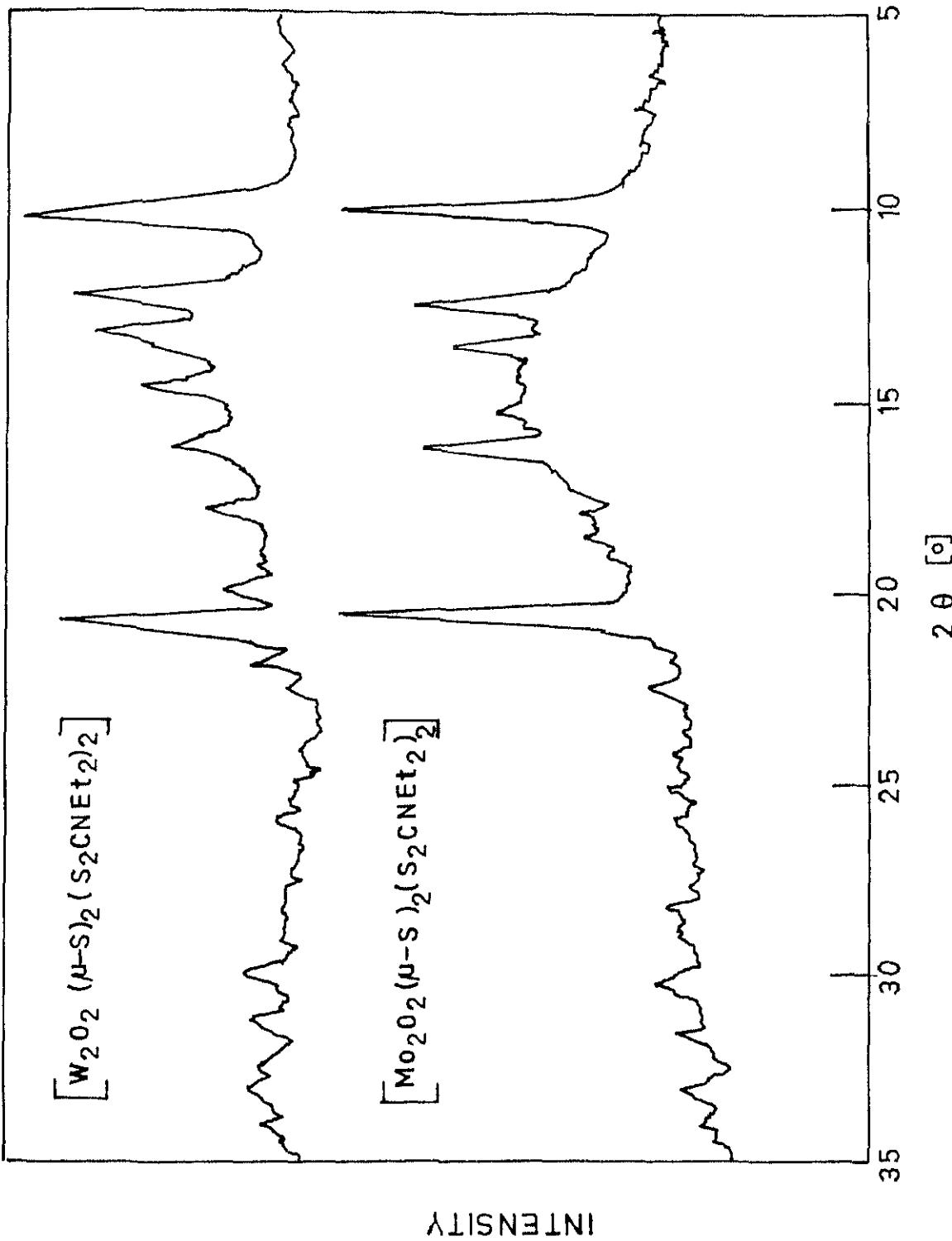


FIG 4.5.8 X-RAY POWDER DIFFRACTOGRAMS

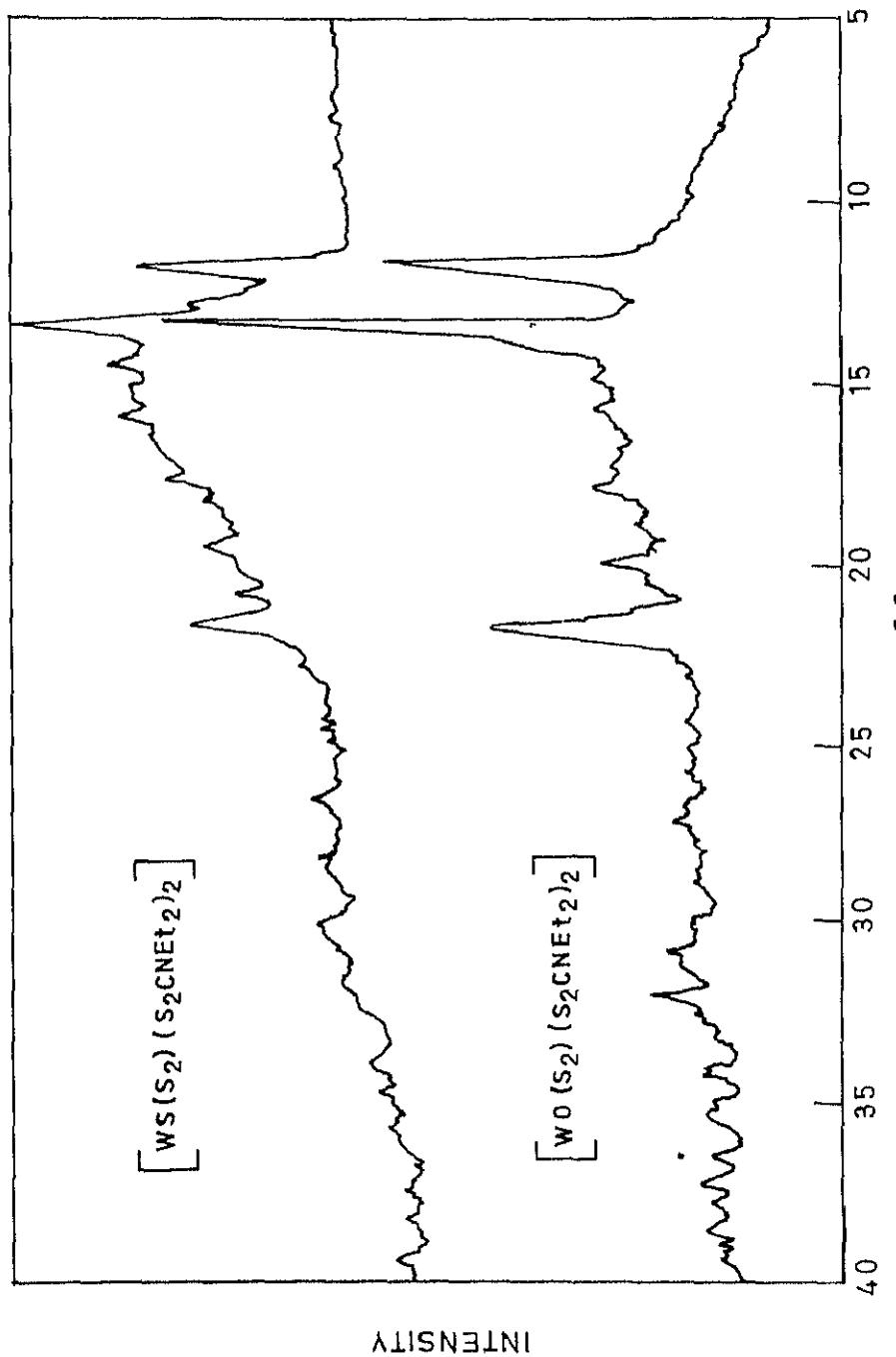


FIG 4.5.9 X-RAY POWDER DIFFRACTOGRAMS

Table 4.13 Summary of Crystal Data

Lattice Dimensions*	$a = 14.500(6) \text{ \AA}$
	$b = 13.434(5) \text{ \AA}$
	$c = 10.174(4) \text{ \AA}$
	$\beta = 105.06(3) \text{ }^\circ$
Volume of unit cell (V)	1913.9 \AA^3
Number of Molecular Units in unit cell (z)	4
Density	1.91 g/cm^3
Space group	$P2_1/C$ (monoclinic)
Radiation	MoK_α (67.90 cm^{-1})

Least squares refinements converged at an R value of 0.060 for 3555 independent reflections [$F_O > 3.92 (F_O)$; $4^\circ < 2\theta < 54^\circ$]

*Values in brackets are the standard deviations

(ET2NH2) [WO(S2)2(ET2DTC)]

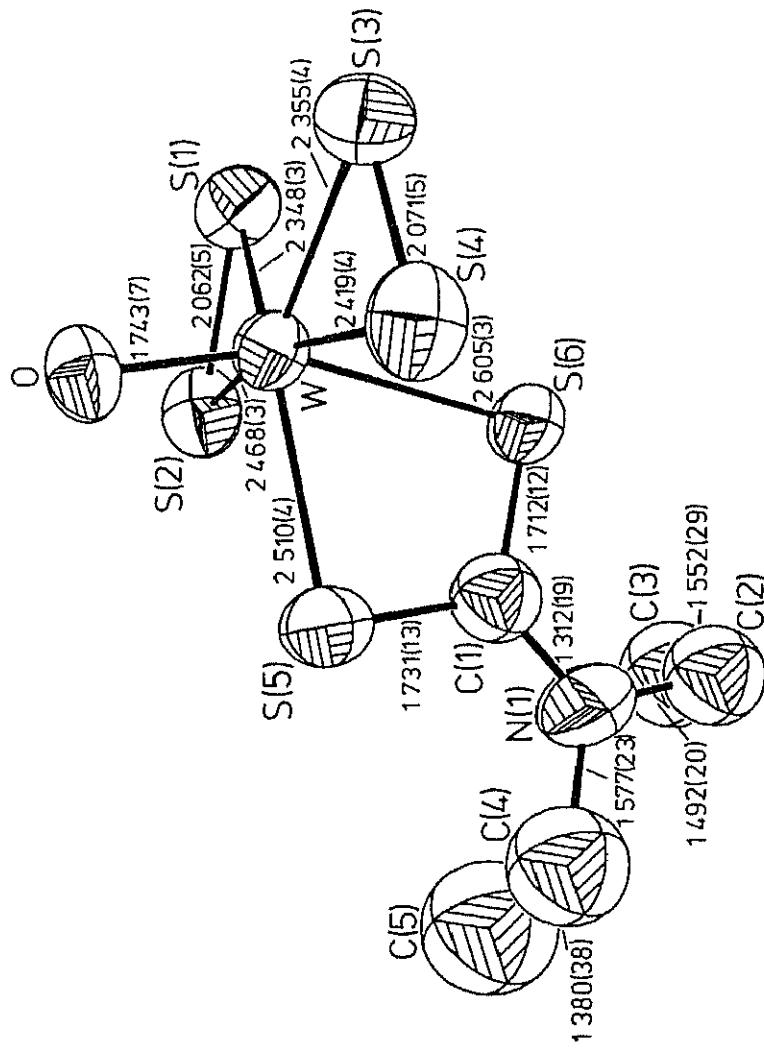


FIG 4.5 10

Table 4.14 Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U
W	2155(1)	457(1)	2347(1)	51(1)*
S(1)	2378(2)	2181(2)	2207(3)	67(1)*
S(2)	2645(2)	1426(2)	581(3)	68(1)*
S(3)	1949(3)	828(3)	4515(3)	76(1)*
S(4)	2093(3)	-676(3)	4168(4)	78(1)*
S(5)	2733(2)	-1049(2)	1337(4)	77(1)*
S(6)	4000(2)	255(2)	3241(3)	65(1)*
O	1008(5)	252(5)	1314(7)	60(2)*
N(1)	4614(9)	-1358(9)	2179(12)	91(5)*
N(2)	486(7)	3984(6)	3509(8)	61(3)*
C(1)	3891(10)	-796(9)	2261(12)	70(3)
C(2)	5609(13)	-1072(12)	2910(16)	96(4)
C(3)	6071(17)	-347(14)	2079(21)	121(6)
C(4)	4438(17)	-2411(14)	1471(21)	123(6)
C(5)	4542(24)	-2228(20)	182(28)	170(10)
C(6)	12(9)	2977(8)	3330(11)	68(3)
C(7)	-216(11)	2680(10)	4619(13)	81(3)
C(8)	742(9)	4388(8)	2294(11)	66(3)
C(9)	1191(13)	5429(11)	2613(16)	93(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 4.15 Bond lengths (\AA)

W-S(1)	2.348(3)	W-S(2)	2.468(3)
W-S(3)	2.355(4)	W-S(4)	2.419(4)
W-S(5)	2.510(4)	W-S(6)	2.605(3)
W-O	1.743(7)	S(1)-S(2)	2.062(5)
S(3)-S(4)	2.071(5)	S(5)-C(1)	1.731(13)
S(6)-C(1)	1.712(12)	N(1)-C(1)	1.312(19)
N(1)-C(2)	1.492(20)	N(1)-C(4)	1.577(23)
N(2)-C(6)	1.507(15)	N(2)-C(8)	1.482(16)
C(2)-C(3)	1.552(29)	C(4)-C(5)	1.380(38)
C(6)-C(7)	1.489(20)	C(8)-C(9)	1.542(18)

Table 4.16 Bond Angles (θ°)

167

S(1)-W-S(2)	50.6(1)	S(1)-W-S(3)	84.3(1)
S(2)-W-S(3)	134.5(1)	S(1)-W-S(4)	134.5(1)
S(2)-W-S(4)	164.9(1)	S(3)-W-S(4)	51.4(1)
S(1)-W-S(5)	134.8(1)	S(2)-W-S(5)	86.4(1)
S(3)-W-S(5)	133.7(1)	S(4)-W-S(5)	83.6(1)
S(1)-W-S(6)	88.8(1)	S(2)-W-S(6)	81.2(1)
S(3)-W-S(6)	93.6(1)	S(4)-W-S(6)	84.6(1)
S(5)-W-S(6)	68.7(1)	S(1)-W-O	104.1(2)
S(2)-W-O	93.1(3)	S(3)-W-O	105.3(3)
S(4)-W-O	98.2(3)	S(5)-W-O	89.7(3)
S(6)-W-O	157.8(3)	W-S(1)-S(2)	67.7(1)
W-S(2)-S(1)	61.7(1)	W-S(3)-S(4)	65.9(1)
W-S(4)-S(3)	62.7(1)	W-S(5)-C(1)	90.0(4)
W-S(6)-C(1)	87.3(5)		

Table 4.17 Anisotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	U11	U22	U33	U23	U13	U12
W	42(1)	56(1)	56(1)	-0(1)	13(1)	0(1)
S(1)	61(2)	58(1)	82(2)	-2(1)	21(1)	-3(1)
S(2)	55(1)	86(2)	66(1)	8(1)	22(1)	-6(1)
S(3)	77(2)	89(2)	67(2)	-2(1)	28(1)	8(2)
S(4)	75(2)	82(2)	78(2)	20(1)	19(2)	-2(2)
S(5)	64(2)	74(2)	90(2)	-24(1)	14(2)	6(1)
S(6)	44(1)	73(2)	73(2)	-12(1)	7(1)	8(1)
O	47(4)	76(4)	54(4)	2(3)	5(3)	-7(3)
N(1)	72(7)	97(8)	103(8)	-23(6)	20(6)	27(6)
N(2)	66(6)	63(5)	58(5)	-1(4)	20(4)	11(4)

The anisotropic temperature factor exponent takes the form.
 $-2\pi^2 h^2 a^* b^* U_{11} + \dots + 2hka^* b^* U_{12}$

The asymmetric tungsten-sulfur distances originating from bound S_2^{2-} is large, consistent with the structural unit in which the sulfur atoms, from two persulfido ligands are approximately trans to each other.^{144,145} Similar asymmetry are found for some O_2 complexes in which the ligand is coordinated side on to the metal.¹⁵⁹

CONCLUSION

Application of Induced Electron Transfer Reactions to tungsten-sulfur systems is a recent phenomenon. Invoking this comparatively newer methodology as synthetic strategy, various mono-, bi- and trinuclear complexes having tungsten in different oxidation states, ranging from +4 to +6 have been synthesized. In some cases, the intermediate species could be identified and probable mechanisms have been proposed. Wherever molybdenum analogs were known, a comparative study has been made. On this basis and other conventional physico-chemical studies, structures of the complexes have been proposed. Only in the case of $(R_2NH_2)[WO(S_2)_2(S_2CNR_2)]$ which does not have its molybdenum analog, assignment of structure, merely on the basis of conventional physicochemical studies was a problem. Thus, the molecular structure of $(Et_2NH_2)[WO(S_2)_2(S_2CNET_2)]$ was determined and the formation of first bispersulfido-tungsten complex has been established.

This work will certainly be of some help to understand the mechanistic and functional aspects of the recently discovered tungsto-enzyme, formate dehydrogenase. Moreover, this is an entirely new approach in synthetic inorganic chemistry. The

field is still in the embryonic stage and many more questions are yet to be answered. Hence, at this stage one then perhaps recalls what Taube said, "At this stage, it would be premature to attribute the difference to effects of the kind we are searching for, but it would be equally premature to give up the search at this stage."

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